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**Electrochemical Advanced Oxidation Process for Shipboard Final
Purification of Filtered Black Water, Gray Water, and Bilge Water**

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**Electrochemical Advanced Oxidation Process for Shipboard Final
Purification of Filtered Black Water, Gray Water, and Bilge Water**

Final Report

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INTRODUCTION

1. Contents and organization of this report

This Final Report summarizes work performed and results obtained over the entire three year term of this project. It consists of two volumes.

While this Final Report was being written, the Contracting Officer's Technical Representative for this project (S.R. Mangum of Carderock NSWC) asked us to describe application of this technology to purifying gray water on a future class of ships, the aircraft carrier presently designated as CVNX. Our response, lightly edited, is attached to this report as Appendix 1 of Volume I. Therein we present our best estimates of how this technology would actually look installed on ship, and how large and expensive it would be. Because the CVNX carrier will be a very large ship, an installation of maximum size is described; a ship with a smaller crew would require an installation that is smaller and cheaper in proportion.

This project advanced the state of the art sufficiently to warrant patent protection. A US Patent Application has been filed, and an identical international patent application; that is, a PCT filing, from which subsequent applications in other countries may be derived. The entire patent application is attached to Volume I as Appendix 2. The reader may refer to it for detailed descriptions of the anodes, procedures for coating them, how needed chemicals are prepared, etc.. The detailed procedures for coating the anodes were in large part developed under this project. The physical design of the electrodes and the basic design of the cell pack predated this project.

The patent application just filed contains a very detailed, up-to-date description of the technology, and it will be placed on open file at the US Patent Office a few months from now. For this reason, there is little in the way of technical information related to the technology itself that we consider sensitive or confidential at this time. The entire first volume of this report, comprising the main body of the report, Appendix 1 (CVNX installation), and Appendix 2 (the patent application) contains no confidential information at all, and may be reproduced and circulated freely with proper attribution of authorship.

Material not protected by the patent applications which we prefer remain confidential for the time being has been segregated in Volume II of this report, which is marked accordingly.

The SERDP Technical Review Committee assigned to us the "Action Item" of producing a plan for transitioning this technology to the US Navy. We have responded to this Action Item in Volume II of this report, wherein we describe the present state of the technology, and our plans for entering commercial production and transitioning the technology to the US Navy for shipboard use purifying waste water. We prefer that our response remain confidential for the time being, because it contains many details of our business plan and manufacturing methods.

2. Technical background

Our electrochemical Advanced Oxidation Process (AOP) utilizes electrodes which generate hydroxyl free radical ($HO\bullet$) by oxidizing water:



Besides the patent application recently filed, this technology is covered by US Patents 5,364,508 and 5,419,824 and 5,439,577 and a patent application is pending in Japan. In our Porous Anode Cell, the anodes are made of Ti-fibers coated with TiO_2 that is heavily n-doped with 4 mole % Nb^{+4} and Sb^{+3} . The Ti-fibers have a very large surface area, providing superior performance at small substrate concentrations.

All substrates tested in the process have been destroyed. The technology is further described in our patents and by Weres (1996, 2000) and Kesselman *et al.* (1997).

This process has a large advantage in regard to energy cost over other Advanced Oxidation Processes. Under realistic conditions (treatment of gray water as described in Appendix 1), and using electrodes that will soon be available (50% current yield), the energy cost is projected to be less than \$5/kg COD removed; the energy cost will decrease as current yield improves. No hydrogen peroxide or ozone is required. Adding about 8% seawater to the waste water would provide sufficient conductivity, if necessary.

The process destroys most organic substances in a nonselective manner, and is expected to find wide application destroying contaminants at COD values greater than other AOPs can handle at reasonable cost. The compact and modular water treatment units make it especially attractive in application to wastes produced at low flow rates in dispersed locations, where conveyance of the waste water to a centralized water treatment facility is impractical. A variety of applications relevant to the needs of DoD and the private sector have been identified:

- (1) Final treatment of bilge water and similar fuel contaminated water after the organic phase has been separated from it by flotation and/or filtration. While the biological treatment process installed at the Craney Island Fuel Depot (Portsmouth, VA) is suitable for shore facilities (Leach and Pearce, 1994), a more compact technology installed on ship would allow bilge water to be treated and discharged while at sea. Our technology is well suited to this application, because the relatively water-soluble organic compounds that predominate in filtered bilge water will be quickly destroyed.
- (2) Final "polishing" of machine shop wastewater after it has been ultrafiltered or otherwise pretreated.
- (3) Final "polishing" of shipboard gray water and black water after it has been ultrafiltered, needed to comply with the treaty requirements of the MARPOL Annex V (NRC, 1996). Test work at Carderock NSWC indicates that membrane filtered black water and gray water still contain too much BOD and COD to allow discharge overboard; therefore,

these waters would still require costly off-loading unless treated. We have run a sample of membrane filtered black water from Carderock with promising results. Implemented as a "polishing" step following membrane filtration, our process will allow the treated wastewaters to be discharged overboard, instead of being stored and off-loaded.

- (4) Detoxification of waste water containing cyanide ion from electroplating operations.
- (5) Treatment of "red water" containing aromatic nitrocompounds from explosives manufacturing.
- (6) Other moderately concentrated waste streams produced at dispersed locations, including pump-and-treat operations, land-fill leachate, pesticide waste, photoprocessing waste, and small waste streams related to chemical or pharmaceutical manufacturing.

3. Reaction mechanism and kinetics

The hydroxyl radicals produced by oxidation of water at the surface of the anode remain loosely attached to the surface of the anode, and the oxidation reaction occurs at the surface of the anode. Depending on the concentration of the substrate in solution, the oxidation reaction may obey first order kinetics or zero order kinetics.

The concept of "reaction order" is fundamental to chemical kinetics:

A "zero order" reaction is one where the rate of disappearance of the reactant of interest is independent of its concentration. When the concentration of the reactant is plotted against time, a straight line is obtained.

A "first order" reaction is one where the rate of disappearance of the reactant of interest is proportional to its concentration. When the concentration of the reactant is plotted against time, a decreasing exponential curve is obtained. When the logarithm of the concentration is plotted against time, a straight line is obtained, with a negative slope proportional to the rate constant of the rate determining step.

When the concentration of reactant is small (in this case, an oxidizable organic compound), and the cell configuration approximates a perfectly stirred reactor, the reaction is first order, and the rate of reaction determined in our tests is given by:

$$R_1 = \frac{dC_s}{dt} = - \frac{A_{anode}}{V} N_{OH} k_s C_s \quad (1)$$

where

C_s = concentration of substrate in solution

t = time

A_{anode} = area of the anode

V = volume of the electrolyte

N_{OH} = apparent concentration of OH^\bullet at the surface of the anode

k_s = the rate constant for reaction of the substrate with OH^\bullet

All reactants consisting of uncharged molecules for which we have clean data appear to obey this kinetic law at low concentration. The slope in a semilogarithmic plot of the data is proportional to $N_{OH}k_s$. The value of N_{OH} can thereby be determined from kinetic data. Butyl Carbitol (diethyleneglycolmonobutylether) is used as the test substrate¹ to determine N_{OH} , assuming that $k_s = 4.1 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$. In determining N_{OH} , the concentration of Butyl Carbitol in solution is determined by gas chromatography.

Note that the first order reaction rate does not depend on the density of current at the surface of the anode. The reaction rate is proportional to the concentration of substrate in solution, and is limited by this value. Current in excess of that required to oxidize substrate molecules at the surface goes to produce oxygen by oxidation of water. Anions in the electrolyte solution may also be oxidized; for example, some chloride is converted to hypochlorite.

Up to a certain point, R increases with C_s , until it reaches a maximum value that is proportional to the current through the cell, and the reaction becomes zero order; that is, independent of C_s :

$$R_0 = - \frac{A_{anode}}{V} \frac{if}{nF_0} \quad (2)$$

where

i = current density at the surface of the anode

f = intrinsic current yield; that is, moles of OH^\bullet produced per mole of electrons passed through the cell

n = number of OH^\bullet required to completely oxidize a molecule of substrate

F_0 = Faraday constant = 96,485 Coulombs/mole

In the zero order kinetic regime, all of the hydroxyl produced by the electrode goes to oxidize substrate molecules in solution, and the slope of COD in solution versus time is proportional to current yield.

¹Buxton et al. (1988) did not provide a rate constant for Butyl Carbitol, and the value used by us to determine N_{OH} ($k_s = 4.1 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$) is an estimate based on tabulated rate constants for related compounds; for example, n-butanol ($k_s = 4.2 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$) and diethylene-glycoldiethylether ($k_s = 3.2 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$).

Current yield is the parameter that describes how efficient the anode is in producing hydroxyl. If all current through the cell went to produce hydroxyl, and all hydroxyl reacted with organic substances in solution, COD would be removed at the rate of 82.9 μ g/Coulomb passed through the cell; this rate of COD removal corresponds to current yield $\varepsilon = 100\%$.

The “threshold concentration” above which the reaction is zero order can be calculated by setting $R_0 = R_I$, and solving the resulting equation for $C_t = C_s$, with the result:

$$C_t = \frac{if}{nF_0 k_s N_{OH}} \quad (3)$$

For a hypothetical “ideal” anode $f = 1$, N_{OH} is large, and

$$R_{ideal} = -\frac{A_{anode}}{V} \frac{i}{nF_0} \quad (4)$$

If $C_s > C_t$ the reaction will be zero order, and the current yield

$$\varepsilon = R_0/R_{ideal} = f \quad (5)$$

The current yield determined under these conditions is the maximum value, and is believed to be an intrinsic property of the anode; therefore, we call it the “intrinsic current yield,” designate it using the symbol “ f ”.

If, however, $C_s < C_t$, the reaction will be first order, and

$$\varepsilon = R_1/R_{ideal} = \frac{nF_0 N_{OH} k_s C_s}{i} = f \frac{C_s}{C_t} \quad (6)$$

Thus, the current yield of the zero order reaction at $C_s > C_t$ is f , while the current yield of the first order reaction at $C_s < C_t$ will be smaller and proportional to N_{OH} and also proportional to C_s .

If the initial value of $C_s > C_t$, the process will initially operate with zero order kinetics and maximum current yield equal to f . When C_s drops below C_t the reaction will continue with first order kinetics, and progressively smaller current yield. The zero order regime might well be considered “heavy clean-up” and the first order regime “final polishing”.

The bottom line is: try to produce electrodes with f and N_{OH} as large as possible, and that is what a large part of this project is all about. Ideally, one would like to make $f=1$ and N_{OH} so large that the process operates mostly in the efficient zero order kinetic regime.

4. Figures of merit, technical objectives, and technical approach

The two parameters f and N_{OH} are legitimate figures of merit describing the anodes, and both

should be made as large as possible. The intrinsic current efficiency f is a direct measure of the energy efficiency of the anodes, while N_{OH} reflects the rate at which contaminants can be removed when $C_s < C_t$. Note that C_t varies inversely with N_{OH} ; therefore, increasing N_{OH} decreases the minimum substrate concentration that can be reached with full utilization of the hydroxyl produced, thereby increasing overall process efficiency. The third important figure of merit is, of course, the useful service life of the anode.

In order of importance to the practical viability of the process

$$\text{Service life} > f > N_{OH}$$

Basically, the anodes have to last a while in service and produce a reasonable amount of hydroxyl if this process is to be practical; improving the kinetics of the oxidation reaction at low substrate concentration is also desirable but not as important.

In fact, the benefits of increased N_{OH} can also be provided by increasing the area of the anode A_{anode} while decreasing current density i in proportion. For this reason, the anodes are made of Ti-metal fiber, providing a rather large anode area. Decreasing current density at the surface of the anode also extends service life by a large factor.

Once it is achieved, the ability to recycle anodes that have failed in service will effectively allow the service life to be multiplied. The number of times the electrodes can be recycled will be limited by cumulative embrittlement of the Ti fiber during the repeated anode coating process. Embrittlement of the fiber depends strongly upon details of the anode production process, and can be quantified by measuring the coated fibers' resistance to breakage under repetitive application of stress. Resistance to breakage is, therefore, a fourth figure of merit for the anodes. In fact, the chemical composition and microstructure of the anodes have changed little since the start of the project. The gradual progress that we have made in regard to increasing f while avoiding major embrittlement has primarily been related to the details of the anode coating process and ever more careful control of process conditions.

5. Microstructure of the anodes and the Task Order of this project

5.1. The layered structure of the anode surface

The anodes are made by applying several layers of metal oxides to the Ti-metal substrate. Multiple layers of the precoat, sealing coat, slurry coat, and overcoat are applied by dipping the anodes in appropriate solutions and baking under a controlled atmosphere. The layered structure of the anode coating is illustrated in Figure 1, and the chemical compositions of the various layers are summarized in Table 1. The details of the process are presented in the patent application, Appendix 2.

The minute fraction of anodic current ($<0.01\%$) that reaches the metallic substrate of the anode through cracks in the oxide coat and the precoat anodizes and passivates the surface of the metal underneath the oxide coat. Passivation of the metal substrate may also cause the oxide coat to

flake off. Both processes cause the cell voltage to increase while N_{OH} decreases, and, eventually, the anode is rendered practically inoperable.

The precoat protects the Ti-metal substrate from passivation. The precoat consists of IrO_2 - Ta_2O_5 in the mole ratio 70-30; these oxides are among the least soluble and most stable substances known to chemistry. This composition is used as an electrode coating by itself, when an anode that produces oxygen at a moderate anodic potential is desired; for example, in electroplating or cathodic protection. Any current that reaches the precoat through defects in the slurry coat is discharged at moderate potential to produce oxygen, thus preventing development of an anode potential at the surface of the Ti-fiber large enough to cause damage by passivation of the metal surface.

A “sealing coat” is applied over the precoat; it consists of SnO_2 doped with 4 mole % antimony. The sealing coat acts as a primer, favoring good adhesion of the slurry coat and thereby preventing bare spots that would allow current to leak through the slurry coat. In fact, this composition (tin dioxide doped with Sb) has itself been used as an electrode coating. An electrode so coated operates at anodic potential high enough to oxidize some organic substances, but with current yield smaller than our electrodes. Thus, contact of some fraction of the sealing coat covered surface with the electrolyte will not depolarize the anode excessively, and the desired high potential is maintained even if there are defects in the slurry coat.

The sealing coat was added just when this project started; adding the sealing coat made it possible to produce precoated anodes with good current yield; without the sealing coat, the current yield of precoated anodes was small. (The electrodes described in the old Weres & Hoffmann patents were made without precoat and worked fine, but only for 20-200 hours.)

The “slurry coat” is derived from an aqueous dispersion of “blue powder,” which consists of TiO_2 particles doped with niobium in the +4 oxidation state to make the TiO_2 semiconductive. The slurry coating composition also contains water soluble compounds of Ti and Sb. When the anodes are dried and heated, the metal compounds decompose to form a cryptocrystalline cement of Sb-doped TiO_2 which cements the Nb-doped TiO_2 particles, producing a soft but adherent “slurry coat.” The Sb-doped TiO_2 is semiconductive as well. The slurry coat provides the main bulk of the oxide coat, and confers a microcrystalline structure which is essential to good anode function and longevity.

The overcoat is derived from an aqueous solution containing titanium glycolate and antimony tartrate, both of which we produce ourselves. The overcoat cements and seals the slurry coat by depositing additional Sb-doped TiO_2 cement between the particles of blue powder.

The electrochemical properties and electroactive surface area of the outer surface affect the anode potential and determine the value of N_{OH} .

The metallic substrate of the anode consists of nominally chemically pure titanium (Ti-Gr.1) in the form of a metallic yarn or tow (the proper name for it), comprising 200 fibers of flattened cross-section with area equal to a circle of 25 μm diameter. Anode life is limited primarily by processes within the metal substrate and its interface with the oxide coat.

It is possible to recondition an anode that has reached the end of its useful life by removing the residual oxide coating and recoating it at a fraction of the cost of replacing the anode. Unfortunately, the process of coating and annealing embrittles the metal, and embrittlement limits the number of times that an anode may be reprocessed. Electrodes made of coated Ti-fiber are particularly susceptible to embrittlement.

The use of antimony as the doping element in the overcoat in place of niobium allows the slurry coat and overcoat to be baked-on under much milder conditions than would otherwise be required. The Sb-doped titanium dioxide that comprises the cement is conductive even when annealed under an atmosphere of argon or carbon dioxide at 450°C. The fiber is hardly embrittled under these relatively mild process conditions.

5.2. Task order of this project

The Task order of this project reflects the layered structure of the electrode coating outlined above.

Improve testing & characterization of anodes:

1. Improve test methods for anodes.
2. Characterize structure of metal, oxide, surface.
3. Develop theoretical model of anode function.

Improve structure & production of anodes:

4. Select best Ti-alloy, optimize annealing & reprocessing.
5. Optimize precoat to improve service life & control costs.
6. Optimize sealing & slurry coats to improve current yield.
7. Improve overcoat for better kinetics.

Improve anode utilization:

8. Identify best operating conditions; control damage by F, etc.
9. Optimize cathode composition and cell configuration to limit “trash” reactions.

6. Design of the anodes

The hydroxyl radicals are produced, and the oxidation reaction takes place at the surface of the anode. At low substrate concentrations, the rate of oxidation becomes proportional to the

product of the anode surface area and the concentration of the substrate in solution; that is, first order kinetics. For this reason, good performance in oxidizing substrate compounds present at low concentration requires the largest surface area that can be provided. Increasing the surface area of the anode also decreases the density of current at the surface (measured in amperes per square meter or milliamperes per square centimeter), thereby decreasing the operating potential of the anode and the cell voltage, and increasing the service life of the anode. For these reasons, the largest possible surface area is preferred, and is provided by using Ti-fiber as the substrate. We use a 200 count Ti-fiber yarn (more properly called “tow”) with a nominal fiber diameter of 25 μ m which was produced by Micrometal Fibers Inc. of Gahanna, OH. Various anodes made using this material have been coated and tested; the major anode types are illustrated in Figure 2.

The full-sized plate anodes are used in our large prototype water treatment units, and we expect to continue using anodes of this kind when the technology is commercialized. At either end, the anode plate has holes for screws and larger holes that serve as channels for water flow perpendicular to the anode plate. (The holes are not shown in this drawing, but they are shown in Fig. 2 of Appendix 2, the patent application.) The Ti-tow is wound on the plate with a 1.27 mm pitch (20 turns/inch) using a lathe modified for that purpose. We have an inert gas furnace with internal dimensions of 10 in x 10 in x 24 in (254 mm x 254 mm x 635 mm) and a slightly larger steaming oven that are used to coat these plates. The furnace and oven could each accomodate two “racks” of 8 or 10 plates each.

The other anodes shown are small test anodes used in the laboratory to test coating compositions and procedures. The “tail” anodes are the smallest among them, and have been in use the longest. The “miniplates” are fairly accurate miniature reproductions of the full-sized anodes. The “frame” anodes consist of Ti-tow wound around a rectangle made by bending 0.045 inch (1.14 mm) Ti-wire (sold as welding rod). “Strip frame” anodes are rigid rectangles with the same dimensions as miniplates made by joining strips of Ti-sheet with screws at the corners.

The current yield measured varies with the design of the anode. Historically, “miniplate” electrodes have given us the lowest current yields, and “tails” the highest current yields with the other electrodes (including full sized plates) in between. During the course of this project, current yields from minipates have improved dramatically, and we believe that the different current yield values obtained with the different anode designs are now due to the design of the test cell and other factors that are not actually determined by the design of the anode.

RESULTS OBTAINED

1. Improved test methods for anodes

The work of improving the anodes involved making them with variations in procedure, and testing them. For obvious practical reasons, miniature test anodes were produced and tested in the laboratory rather than full-sized electrodes that we could have made in our pilot plant.

1.1. Improved production of test anodes

For years, we made small test anodes using an ordinary laboratory box furnace. A controlled atmosphere was provided inside a small tubular capsule (1 in D x 4 in L = 25 mm x 102 mm) within the furnace when needed. This set-up allowed only the smallest anodes to be annealed at high temperature, and was able to provide reliable temperature control only at red heat or above, where heat transfer by radiation is effective.

Figure 3 illustrates two laboratory coating ovens built to produce larger test anodes under tightly controlled, more realistic conditions. In both cases, a stainless steel tray serves as the oven chamber. The usable internal volume of the tray is about 6 in L x 4 in W x 4 in D (152 mm x 102 mm x 102 mm). In either case, the tray is inverted on top of a hot plate to provide a chamber that is more-or-less isolated from ambient air. The tray has a thermocouple and heating elements attached to the outer walls, and is wrapped with thick nonwoven silica textile to provide good thermal insulation.

The steaming oven at the top of Figure 3 operates at 200°C with an atmosphere of steam. The large laboratory hotplate has its own temperature control and may be operated up to 300°C. Steam is provided using an external boiler. The jetting action of the steam entering the chamber provides good mixing and uniform temperature within the chamber volume. The baking oven sits on a special high temperature hotplate that was built for this purpose. The actual hotplate was machined from a plate of high density graphite with three horizontal bores for cartridge heaters. Tray is wrapped with a fiberglass insulated flexible heater, and the tray and the hotplate are independently temperature controlled by external controllers.

Having two ovens, we are able to test processes involving a steaming step at about 200°C followed by baking or annealing at a higher temperature, under inert gas if so desired. In either case, the chamber volume is large enough to process two miniplate electrodes or up to eight tail electrodes at one time.

1.2. Endurance testing

1.2.1. Long term testing unit

Figure 4 depicts the Long Term Testing Unit (LTTU) that we use to determine anode life. The design of the LTTU borrowed many details from the water treatment prototypes, and will contribute many features to future prototype units. The LTTU is designed for long-term, low maintenance operation. It is fail-safe and will automatically resume operation after a power-failure. The data acquisition and control functions are completely separate. The Model HP 34970A Data Acquisition unit continuously monitors up to 22 variables and operates independently of the computer; the computer needs to communicate with the DA unit only when the data acquisition program is changed or data must be uploaded. Current, temperature, and

electrolyte conductivity are actively controlled. Low level in the electrolyte reservoir and low flow cause power-down.

Up to twelve anodes may be tested simultaneously, arranged in three groups containing up to four anodes each wired in series; therefore, the cells within each group operate at exactly the same current. Typically, the voltage across each cell and the current through the group are recorded every hour, together with temperature and electrolyte conductivity. The gradual increase of voltage measured across the cell reflects the progressive degradation of the anode. Each cell is provided with an overvoltage protection circuit which short-circuits the cell if cell voltage exceeds a preset limit, typically set to ten volts.

Determining the service life of anodes designed for at least three months service life is inevitably a time consuming business. The tests may be run at increased current density, typically 2X or 4X the nominal rating of the electrode, in order to accelerate wear and allow the test to be concluded in a shorter period of time. The LTTU includes two current controlled DC power supplies; therefore, tests at two different values of current can be run at the same time.

The first set of “tail” electrodes were run for over 1400 hours (that is, nearly two months) in the LTTU. This run served to shake down the unit, and generated some interesting test results. For example, it was noted that stainless steel cathodes would sooner-or-later corrode if operated in sodium chloride electrolyte, and it was ultimately decided to go to Hastelloy C-22 cathodes in full-sized units as well as in the test cells (Section 9).

An off-white “crud” was observed depositing on the working face of the cathode. This crud appeared to be a mixture of clay and plastic particles derived from gradual decomposition of white PVC plastic in the system, which is very likely filled with a white clay. Initially, the cooling tower section of the LTTU was filled with 1 inch (25 mm) PVC Raschig rings made by cutting 1 inch white PVC plastic pipe into 1 inch pieces. The deposition of crud on the cathodes was eliminated by replacing the white PVC Raschig rings with polyethylene rings, and a filter was added to the system. We subsequently eliminated the cooling tower packing entirely from the design of the large prototype water treatment units, which already included water filters. In Model 3.10, PVC will be limited to just a few pipe fittings that could not be procured in polypropylene at a reasonable cost.

1.2.2. Summary of anode test results

Several sets of tail electrodes have been run in the LTTU in tests extending up to 1500 hours. The LTTU has also been extensively used to run short tests (less than one day) using four or eight electrodes to determine N_{OH} or current yield.

There is much variability in the test results, even when using electrodes that were prepared together and should be identical. The variability is certainly aggravated by the small size of the “tail” electrodes, which contain only about a gram of Ti-fiber. In large electrodes, variations among different parts of the electrode will, of course, tend to average out.

One of two electrodes operated at 4X current density for 920 hours came out of the test with

normal values of operating voltage and current yield, while its mate failed at 450 hours due to high voltage, indicating passivation of the metal surface beneath the coating. This result suggests that prolonged operation at 1X current density should be possible with large electrodes. If some portions fail by passivating, the remainder of the fiber will continue to function, and the electrode will keep working, albeit at higher voltage.

No electrodes tested at 1X or 2X current density failed by passivation. Some of them continued operating for hundreds of hours at normal voltage, and with good current yield at the end of the test. Two electrodes did, however, fail by losing current yield at constant or slightly reduced operating voltage at the end of the test, suggesting development of cracks that extend through the slurry coat and allow electrolyte to contact the precoat. If this kind of failure affects parts of a large electrode, it will be manifested by a gradual decrease of N_{OH} with operating time.

Happily, failed electrodes can be reprocessed. Overall, these test results indicate that full-sized electrodes will probably last at least 2-3 months in service while their properties gradually deteriorate. The prospects for successful reprocessing appear good, and there are indications that, in the case of electrodes that deteriorated by loss of current yield, the reprocessed electrodes seem as good as the new electrodes (Section 4.1.3 below).

The few times that we have made and tested large electrodes, the appearance of the coating has usually been rather better than the appearance of tail electrodes or miniplates, and the test results comparable to or better than “typical” tail electrodes or miniplates. Better quality of the product is to be expected, because the process of coating the large electrodes is inherently more stable and uniform due to the much larger size of the electrodes, which are typically coated in batches of seven to ten electrodes.

1.3. Measurement of N_{OH}

The choice of method and substrate for measuring N_{OH} proved to be a continuing source of vexation. As described in the Introduction, N_{OH} is the parameter that describes the anode's chemical kinetics; it has the dimensions of moles $OH\cdot$ per centimeter squared, and may be interpreted as representing the steady state concentration of hydroxyl radicals bound to the surface of the anode.

Because the performance of the anodes at low substrate concentration is dominated by the value of N_{OH} , it is an important figure of merit that must be determined as part of the routine testing and evaluation of the anodes as they are produced. The determination of N_{OH} is therefore done routinely and frequently, and must easily produce reproducible data.

Among analytical techniques available to quantify the concentration of specific organic compounds in solution, absorption spectrophotometry is by far the easiest: just pipette a sample into the cuvette, put it in the spectrophotometer, and record the optical density. Improved sensitivity and accuracy is obtained by measuring peak-to-peak heights on a derivative absorbance spectrum at small cost of increased complexity and time. Most aromatic compounds have usable absorption peaks in the ultraviolet, and a few colored compounds absorb in the visible. We have an a first rate - albeit ancient - dual beam UV-Vis-NIR spectrophotometer in

our laboratory, and tend to use it whenever possible.

The ease, sensitivity and accuracy of UV absorption spectrophotometry made the technique seductively attractive and, in retrospect, we relied on it too much. The basic problem is that the technique is practically limited to aromatic compounds (which absorb strongly in the UV). Also, in order to determine N_{OH} , the reaction rate constant of the particular substrate with hydroxyl must be known. Unfortunately, aromatic compounds are rather reactive: they react very nicely with hydroxyl radical but, unfortunately, they also react in all sorts of other ways.

Years ago, we started by determining N_{OH} using p-cresol as the substrate; p-cresol has the additional advantage of reacting very rapidly with hydroxyl, whereby N_{OH} could easily be determined using the plate electrodes we were using at the time, which have much smaller surface area than the fiber electrodes. Initially, we were doing most tests in dilute NaCl electrolyte, as NaCl is likely to be the electrolyte present in many applications. Invariably, p-cresol disappeared very rapidly in NaCl electrolyte, suggesting a large value of N_{OH} . Unfortunately, other substrates did not go away at nearly the rate predicted by comparison with p-cresol. After months of aggravation, it was discovered that sodium hypochlorite, a reaction byproduct produced by oxidation of the NaCl electrolyte, was reacting with the p-cresol converting it to a compound that was tentatively identified as methyl-2,4- benzoquinone. Because hypochlorite is a stable species that was released into the solution, the oxidation of p-cresol was quite rapid. Unfortunately, the reaction stopped with the benzoquinone, which is nearly as toxic as cresol.

Subsequently, we eliminated interference from hypochlorite by using sodium bicarbonate as the electrolyte - together with cresol - to determine N_{OH} . Aside from being essentially noncorrosive, sodium bicarbonate is easily maintained at constant pH by bubbling carbon dioxide through it. We were able to determine reproducible values of N_{OH} in sodium bicarbonate, but we never quite trusted the results. Something goes on in sodium bicarbonate that confounds the determination of current yield; typically, the change in COD observed in sodium bicarbonate electrolyte is small and erratic, and sometimes the COD actually increases. These observations made us wary of values of N_{OH} determined in sodium bicarbonate as well. In particular, we were concerned that the apparent value of N_{OH} seemed to decrease as the reaction progressed. Also, with Ti-fiber electrodes p-cresol is destroyed so rapidly that the reaction becomes difficult to follow, and we were also concerned that mass transfer might become the rate limiting phenomenon instead of the chemical kinetics that we were trying to measure.

In order to decrease the reaction rate and, we thought, to decrease the possibility of spurious side reactions, we eventually replaced p-cresol with benzaldehyde, which reacts about three times less rapidly with hydroxyl, allowing larger values of N_{OH} to be conveniently measured. While benzaldehyde is less convenient to use than p-cresol in that it is less soluble in water, unlike p-cresol, benzaldehyde presents essentially no toxic hazard; benzaldehyde is, after all, the food additive that gives almond cookies their characteristic aroma. The values of N_{OH} obtained with benzaldehyde were generally slightly larger than those obtained using p-cresol, and they tended to increase with reaction time rather than decrease.

We started using benzaldehyde in sodium bicarbonate electrolyte. Soon, the values of N_{OH} that we were obtaining dropped precipitously. Frantically, we tried varying or “correcting” this and that, but to little avail: we remained unable to reproduce the best values of N_{OH} that had previously been obtained. After months of frantic effort, we finally realized that the high values which we had sometimes obtained with benzaldehyde were due to a specific reaction of benzaldehyde, and this reaction appeared to be powerfully affected by subtle variations in the chemical composition of our tap water which we were using to prepare the solutions. Tests run in solutions prepared using deionized water gave consistent, albeit much smaller values for N_{OH} , which reflected the actual rate of reaction of benzaldehyde with hydroxyl at the surface of the anode. These values of N_{OH} were too small to reconcile with the p-cresol data. Ultimately, we concluded that bicarbonate was interfering with the oxidation of benzaldehyde.

Ultimately, we gave up on aromatic test substrates all together, and started using diethyleneglycolmonobutylether as the test substrate. This rather boring aliphatic compound is occasionally used as an industrial solvent, often under the trade name Butyl Carbitol®. We purchased a better Flame Ionization Detector for our gas chromatograph, and are now able to analyze Butyl Carbitol at concentrations small enough to be of use in determining N_{OH} . Using Butyl Carbitol in 0.04N NaCl, we were finally able to get reproducible values of N_{OH} . We believe these values to be true, as Butyl Carbitol has no specific chemical reactivity (as aromatics do), and NaCl is the least obtrusive electrolyte that we have been able to identify.

The moral of the story is: use a “difficult” substrate to quantify process performance because the easy, more highly reactive ones are likely to be destroyed by assorted side reactions.

2. Characterization of metal, oxide coating, and surface properties

Samples of the coated fiber were sent to a commercial electron microscopy laboratory (Technology of Materials, Santa Barbara, CA) for analysis. All stages of the coating process were represented, from bare fiber to completed anode. A sample of coating scraped from a plate electrode was also provided.

2.1. X-ray diffraction

X-ray diffraction analyses of coating scraped from a coated plate anode showed the composition to be predominantly anatase with crystallite size of about 0.14-0.16 μ m plus a smaller amount of rutile. The indicated size corresponds to our estimates of the ultimate particle size in our “blue powder.” XRD analysis of a coated fiber anode revealed titanium metal, a smaller amount of anatase, plus a substantial amount of an unidentified amorphous phase which is most likely the glassy “cement,” derived from the overcoating solution, which binds the particles of “blue powder” to produce a cohesive oxide coat. These results are consistent with our expectations: the oxide coating consists of fine particles with the crystal structure of anatase, cemented by a amorphous or cryptocrystalline cement. The particles are, of course, doped with Nb⁺⁴, and the cement is doped with Sb, rendering both phases conductive.

2.2. Coat morphology and surface analysis

The SEM photos have been presented in the Annual Report for FY 1998, and will just be summarized here. The bare fiber has a very rough surface texture, with pronounced ridges and deep gullies parallel with the axis of the fiber. This texture is obviously an artifact of the composite drawing process². Elemental surface analysis indicated very little iron contamination remaining from the composite drawing process; therefore, iron contamination is not the cause of variable current yield or variable N_{OH} .

An image collected in “back scatter emission” mode (BSE) shows that the precoat quality varies greatly from fiber to fiber. In BSE mode, heavier elements look bright in the image; thus, brighter appearance indicated a thicker deposit of Ir and Ta forming a thicker precoat. A few of the fibers appeared uniformly brighter than the others, indicating a thicker precoat. The observation that the variation along the surface of any single fiber is much smaller than the variation among fibers indicates a mechanism that affects entire fibers rather than patches on the surface of a fiber. This pattern suggests that an electrochemical process is controlling deposition of the precoat.

BSE images of the seal-coated specimen showed similar variations from fiber-to-fiber. At this stage, the variations were even more pronounced. The surface striations on the brighter fibers were nearly filled with solid deposits, while striations on the less bright fibers were partially filled. We believe that the electrochemical process at work is depassivation of the fiber surface in the 3N HCl precoating solution. The striations are filled with deposits that contain the oxides of Ir and Ta from the precoat together with titanium dioxide derived from titanium chloride that is produced by corrosion of the metal surface. Some fibers are strongly depassivated, and a large amount of the mixed oxide is deposited, while others are hardly depassivated at all, resulting in a thin precoat which is indicated by a dark appearance in these images. This interpretation of the variability observed led us to a simple modification of the precoating process which did, in fact, give us better anodes (Section 5).

A close-up SEM image of a slurry coated fiber revealed a slurry coat with a very clumpy texture, which probably is porous. The SEM image of completely coated fibers (including overcoat) showed that the coating is quite uneven in addition to being porous. These results, obtained using electrodes prepared at the start of this project, confirmed that work was needed to improve the quality of the oxide coat. We routinely monitor the appearance of the coated fibers using a metallographic microscope to monitor the appearance of the anodes as we are coating them; that

²The fibers are produced by hot rolling then drawing a composite of titanium wires imbedded in a carbon steel matrix. Numerous holes are drilled lengthwise through a cylindrical ingot of carbon steel, and a rod of titanium of diameter just smaller than the holes is placed in each hole. This composite is hot rolled into a bar, and the bar is drawn into a wire. While the steel ingot is transformed into a stout steel wire, the titanium bars imbedded in it are transformed into the small fibers desired. The drawn composite wire is then wrapped on to a stainless steel mandrel and dipped into a warm solution of nitric acid. The acid easily dissolves the iron, but doesn't touch the titanium or the stainless steel. The Ti-fiber tow is then rinsed to remove the acid and dissolved iron and dried, and finally transferred to plastic spools for shipment. We receive it in that form.

is, an optical microscope that operates in reflected light mode as needed to examine opaque specimens. These observations indicate that the improved coating procedure now used gives a more uniform slurry coat.

2.3. Electrical properties of the oxide code

Previously, we were unable to make the sophisticated electrical measurements needed to properly characterize the anodes and provide input data to the theoretical modelling effort; for example, the capacitance of the anode-electrolyte interface, which should be proportional to the active surface area.

A system of hardware and software suited to this purpose has been developed and is fully operational. It is illustrated in Figure 5. The critical piece of hardware is the ramp generator, which produces an exponential voltage curve wherein the initial voltage, final voltage, and time constant are adjustable. An AC signal generated by a function generator is superimposed on the DC ramp, and the composite signal is provided to the potentiostat. The potentiostat applies this potential to the anode in the test cell. DC signals proportional to anode potential and voltage are transmitted back to the ramp generator, which displays them on digital meters and relays them to a two channel, 12-bit A/D converter. The digitized signal is then transmitted to a laptop computer running a data acquisition program, and is ultimately stored on a diskette.

A data analysis program running on a desktop computer determines the amplitude and phase angle of the current through the cell relative to the anode potential, and prints a table of DC impedance (Z_{dc}), and complex AC impedance (Z_r and Z_i) as a function of DC potential applied (that is, the ramp voltage). This program also fits a three parameter equivalent circuit to the three measured impedance values. All quantities are measured and calculated as a function of DC potential applied to the anode (that is, the ramp voltage) at a fixed frequency.

The test cell is enclosed in a Faraday cage to minimize electrical noise entering the reference electrode loop, which is extremely sensitive to noise because of the very high input impedance of the potential sensing circuit ($> 10^{10}\Omega$). The remaining high frequency electrical noise in the system is less than 2mv p-p, which is insignificant when an AC signal of 100 mV p-p is applied.

The familiar problems maintaining a stable electrolyte level in the reference electrode chamber and avoiding bubbles in the Luggin capillary (that is, the tube connecting the reference electrode chamber to the test cell) were solved by pressurizing the test cell with pumped electrolyte, whereby the Luggin capillary flowed upwards, and the level in the reference electrode chamber is stabilized by overflow with no operator attention required. The centrifugal pump is installed in a separate metal box in order to eliminate electrical noise from the pump. With appropriate test cells installed, this system can be used to test either tail electrodes or miniplates.

The ramp generator and the entire test cell/ Faraday cage assembly were designed and built in-house. The data analysis program was also written in house, in FORTRAN. The other components (function generator, potentiostat, A/D convertor, computers, data acquisition program) are all commercial items, most of which predated this project.

2.4. Test of fiber brittleness

The simple device built for measuring the brittleness of the coated Ti-tow is shown in Figure 6. A length of coated Ti-tow is pulled back-and-forth over a small metal pulley at constant tension while the number of cycles is counted. When the sample breaks the machine stops, and the number of cycles required to break the fiber may be read from the counter display.

3. Theoretical model of anode function

Electrochemists have produced a variety of theoretical models of the electron transfer process at the surface of an electrode. The model of electron transfer at the surface of n-doped SnO_2 developed by Memming and Möllers (1972) is most directly applicable to our electrodes. This model ignores the effect of ions in the electrolyte, but it does describe the tunneling of electrons through a depletion zone at the surface of a semiconducting electrode in a numerically tractable way.

These electrode models sometimes consider the influence of ions in the electrolyte upon charge distribution at the surface of the electrode in a rudimentary manner. These models rarely (if ever) go beyond representing the ion distribution as a diffuse double layer (the Gouy-Chapman Theory), or a diffuse double layer plus a Stern layer; that is, a partial layer of ions right at the surface of the electrode (the Stern Model). The diffuse double layer submodel is correct as far as it goes, but the Stern layer submodel can, at most, adequately represent ion absorption of ions on an oxide-free metal surface; for example, platinum or mercury at moderate potentials. An oxide-free metal surface approximates a flat and featureless plane of diffuse charge; therefore, absorption of oppositely charged ions is determined by how many ions can crowd together at the surface; in other words, the Stern layer. The Stern model is totally inadequate to describe ion exchange at the surface of a metal oxide covered electrode, where the surface is populated with discrete acidic and basic sites which exchange protons and hydroxide ions with the electrolyte as a function electrode potential and pH, and provide discrete sites for chemisorption of ions.

On the other hand, geochemists and surface chemists have generated a variety of detailed models describing ion exchange on mineral surfaces and similar metal oxide materials; for example, see the review by Davis and Kent (1990). The so-called “three layer” model in the form proposed by Davis *et al.* (1978) allows the simultaneous adsorption of different ions on a metal oxide surface to be fitted and calculated. The three layer model has the additional advantage that many researchers have used it to fit their titration data; therefore, the fitting parameters appropriate to many metal oxides and ions are available in the literature, including TiO_2 .

Of course, a rock is not an electrode, and the models developed by geochemists do not allow the solid phase to have a charge (that is, there is no depletion zone) and electron transport through the surface isn't considered.

We produced a more sophisticated model of the surface of our anodes and how they function by combining the electron transfer model of Memming and Möllers (1972) with the surface charging/ ion complexation model of Davis *et al.* (1978). The combined model allows the effect

of electrode potential upon surface ionization and ion complexation to be calculated, as well as the effect of ion adsorption upon electron transfer. In the process of combining the two models, we improved upon them individually. An error of derivation was corrected in the model of Memming and Möllers. The model of Davis *et al.* represents the diffuse double layer by an analytical expression which describes only pure symmetrical electrolytes; for example, a solution containing NaCl and nothing else. We elected to compute the properties of the diffuse double layer allowing an arbitrary mixture of different ions of different charge types.

This entire model is embodied in a computer program written in FORTRAN which runs nicely and quickly on a desk computer. The program was completed toward the end of this project. The entire program has been debugged, and charge distributions and ion exchange have been calculated as a function of anode potential and pH using model parameters from the literature. The electron transfer part of the model also works, but needs to be fitted to our own electrode test data; there is no literature data to rely on in this case.

The model immediately revealed an unexpected phenomenon at the surface of the anode. When a positive potential is applied to the anode, more cations are attracted to surface than anions; the Stern Model commonly used by electrochemists predicts the opposite, as does “common sense.” Anodic polarization of the anode creates a substantial positive space charge just within the surface of the electrode; that is, the depletion layer. Protons are released from the surface of the anode, creating a compensating negative charge in the Inner Helmholtz Plane (IHP). Thus, the electric potential at the IHP and at the Outer Helmholtz Plane (OHP), where counterions are located, is still positive, but much smaller than it would be otherwise. The OHP contains a substantial excess of cations over anions, because cations are chemisorbed to the negatively charged surface sites in the IHP. The net positive charge in the OHP is balanced by a net negative charge in the diffuse double layer. In summary, the charge distribution at the interface consists of four distinct layers: a positive depletion layer within the solid, a compensating negative charge in the IHP due to loss of protons, a positive charge in the OHP due to chemisorption of cations, and a compensating negative charge in the diffuse double layer. A calculation based on the Stern Model traditionally favored by electrochemists would have predicted something rather different: a positive depletion layer, a negative Stern layer, a negative diffuse double layer, with cations nowhere to be seen.

4. Choice of Ti-alloy, annealing and reprocessing

Embrittlement of the Ti-fiber during processing and reprocessing imposes the ultimate limit on electrode life, and must be minimized.

4.1. Annealing and reprocessing methods

4.1.1. Fiber embrittlement during processing minimized

There have been two major improvements in electrode processing as far as embrittlement of the metal is concerned.

Just as we were starting this project, we discovered that, if the overcoat was doped with Sb instead of Nb, baking the electrodes at 400-450°C would impart adequate (semi)conductivity to the oxide coat. By eliminating the final annealing step at 600-750°C, which is needed to render Nb-doped overcoat conductive, we greatly reduced embrittlement.

The second major improvement was a preliminary steaming step at 200°C to remove glycolic acid and other organic constituents of the coating composition and minimize the formation of char. Removing the organics at 200°C eliminates the need to expose the anodes to air or steam at 450°C to remove organic residues, thereby further decreasing embrittlement.

Other, smaller, process changes provided further improvements in the quality of the product. For example, immediately after they are removed from the steaming chamber at 200°C, the anodes are dipped into water, then placed in the annealing chamber at 450°C, wet. The initial thermal shock separates the fibers glued together with overcoat, and the blast of steam generated in the 450°C furnace quickly sweeps air from the furnace chamber. The steam, initially at 100°, is then quickly removed by CO₂ or, preferably, argon. Minimizing exposure to air (which is much worse than steam) and to steam at 450°C further diminishes embrittlement.

At the start of this project, it was possible to break the coated fiber by pinching it between fingernail and finger, and the electrodes rapidly became ratty looking with broken fibers when handled. Now it is impossible to pinch off fiber, and no broken fibers are apparent. The prognosis is excellent.

4.1.2. Current yield improved

Continuous improvement of current yield was recorded over the duration of this project.

In December 1998, just before we figured-out to how to eliminate residual “char” from organic compounds in the coating compositions, the current yield of miniplates typically ranged 3-8%. In March of 1999, after we started “steaming” the electrodes to eliminate char, miniplates were coming in at 13% current yield.

By mid-May of 1999, our best miniplates had reached 28% current yield. By January of 2000, our better miniplates ranged 25-35%.

The following factors and improvements have enabled this large increase in current yield:

1. Steaming the electrodes at 200°C to remove organic materials before baking them at 450°C has greatly reduced the amount of organic matter remaining in the oxide coat.
2. Dipping the electrodes in water before putting them into the 450° baking chamber eliminates damage from exposure to air at 450°, and “fluffs” the fibers, eliminating the need to fluff the fibers mechanically between coats.
3. “Breaking in” the electrode by operating it for 2-4 days eliminates the traces of organic matter remaining, increasing current yield.

4. Replacing stainless steel cathodes with Hastelloy cathodes has almost eliminated corrosion of the cathodes, and has prevented the decrease in current yield associated with corrosion products suspended in the electrolyte (Section 9).
5. When electrolyte pH is controlled to keep it near to 5.5, the current yield is higher than at the higher pH values typical of NaCl electrolyte without pH control (Section 8.3).

Note that points 4 and 5 relate to controlling factors external to the anode. We expect that further increase of current yield will come from optimizing operating conditions, the geometry of the anode (discussed below), and the composition of the cathode.

Current yield is strongly affected by the geometry of the anode, all else being equal. Table 2 compares electrodes of different geometries, but coated in the same way. Tail electrode 1 has much larger current yield than the frame electrode 2 or the miniplate 3 made using the same fiber. A tail made from fiber taken off of frame electrode 2 had current yield slightly greater than tail 1; thus, the effect of geometry is expressed when the electrode is operated, rather than when it is coated. Tail 10, made using 400 count tow, had substantially lower current yield than tail 1, made using 200 count tow, and frame electrode 2 had larger current yield than miniplate 3. These comparisons all suggest that “fluffier” electrodes, with better access of electrolyte to coated fiber do better. This observation suggests that full sized plate electrodes, where the length of fiber is 8 inches versus 2.25 inches in the miniplates should have larger current yield, because increased cementation, etc., that occur towards the edges of the plate should have less effect. Also, the full-sized electrodes are mounted in a cell that guarantees good electrolyte contact and circulation.

The results summarized above lead to an important conclusion which bears on the direction of our further research: with the possible exception of tail anodes, the composition and microscopic structure of the oxide coat may no longer be the factors limiting current yield. The design of the anode, and the conditions under which it is operated appear to be more important.

4.1.3. Reprocessing methods

During the course of this project, various electrodes failed or were damaged in various ways, and were reprocessed. The procedures are straightforward:

- (1) If the anode is contaminated with iron, it can be cleaned by soaking in a warm, dilute solution of citric acid. If iron contamination was the only problem, nothing else needs to be done.
- (2) If the anode is losing its coating, sonicate it to remove the defective coating, then apply sealing coat, slurry coat, and overcoat as for a new anode.
- (3) If the anode has lost conductivity (indicated by high cell voltage), anneal it under argon at 700°C for one hour, then apply at least one slurry/overcoat cycle.

- (4) If the anode has lost current yield but cell voltage is normal or low, apply a single cycle of slurry and overcoat.
- (5) After recoating, break-in the reprocessed electrode by operating it in NaCl electrolyte for a few days.

In all cases, the reprocessed anode will be operable, with current yield at least as good as when the anode was brand new. If the anode had failed by losing conductivity, conductivity will be restored, although the anode may operate at a noticeably larger cell voltage. Otherwise, the cell voltage of the reprocessed electrode should be normal.

Thus, it appears that embrittlement of the Ti-fiber from repeated cycles of reprocessing will pose the ultimate limit on the useful life of the anodes. Because the degree of embrittlement is now small, it should be possible to reprocess the anodes several times.

4.2. New Ti-alloy not needed

At the start of this project embrittlement was a major issue. We thought to special order Ti-fiber tow made of one of the harder Ti alloys on the expectation that a harder alloy, with smaller crystals in the metal, would be less susceptible to embrittlement. However, review of the literature on Ti-alloys and conversations with Carderock staff who worked with Ti-alloys in the context of submarine hulls revealed that the harder Ti-alloys would be much more susceptible to pitting. Because pitting tendency would be deadly in a coated anode, we decided to stick with Ti-Gr.1 as the fiber material; that is, nominally chemically pure Ti.

5. Improved precoat

Precoated Ti-fiber tow was found to contain individual fibers of markedly different appearance (Section 2.2). Some precoated fibers had the same surface texture as uncoated fiber, indicating a thin, uniform precoat, and no corrosion of the Ti-metal during the precoating process. Other fibers had thick coats that completely filled-in the grooves on the surface of the fiber, suggesting a thick coat composed, in part, of titanium oxide derived from corrosion of the metal. These results were obtained using a precoating solution wherein 3N HCl served as the solvent. Apparently, some fibers remained passive and didn't corrode, while others corroded, producing the large variations observed.

Manipulating the degree of passivation of a metal surface to control corrosion is a familiar problem in corrosion science. HCl is a reducing acid which favors depassivation and corrosion, but the tantalum and iridium salts in the precoating solution are mild oxidizing agents and tend to counter the corrosive effect of the HCl. A solution of HCl in n-butanol is strongly reducing, and will favor depassivation and corrosion of Ti-metal. On the other hand, adding an oxidizing agent (for example, nitric acid) to HCl solution will give it an oxidizing character, passivating the metal and blocking corrosion to produce a thin, uniform precoat consisting of tantalum and iridium oxides with little or no titanium dioxide present.

A series of six frame electrodes were prepared, differing only in the precoat applied. The matrix tested two factors:

(a) Metals in the precoat solution:

- (i) 70 Ir - 30 Ta
- (ii) Ir only

(b) Choice of solvent:

- (i) n-butanol with HCl added
- (ii) 3N HCl
- (iii) 3N HCl with 2% nitric acid added; this mixture of acids falls within the range of compositions traditionally called "aqua regia."

The precoat anodes were examined with an optical microscope, the coating cycle was completed, and the anodes were tested. The two anodes that looked best after precoat were Ir-Ta in aqua regia, and Ir-Ta in n-butanol. Overall, these electrodes also had the best test results when completed.

The corrosive, n-butanol based, precoat probably produced a uniformly thick precoat. Precoat solutions based on n-butanol or another alcohol are preferred in the literature, probably for this reason.

The passivating, aqua regia based, precoat probably produced a thin and uniform precoat. Inhibiting corrosion eliminates the gross variation from fiber-to-fiber. Aqua regia is the only agent that can dissolve iridium metal and iridium dioxide; therefore, the iridium probably remained in solution longer as the precoat solution was boiled down, favoring deposition of a more uniform precoat. Test samples precoat with and without nitric acid added to the 3N HCl were sent out for elemental surface analysis using the Auger technique, and the results confirmed that adding nitric acid gives a more uniform distribution of Ir and Ta in the resulting precoat.

In this application, the geometry of the substrate dictates the choice among these two recipes. With the fiber as thin as it is, corrosion risks fiber breakage and embrittlement; therefore, a thin precoat without corrosion of the metal is to be preferred, and we have selected Ir-Ta in 3N HCl with nitric acid as the best precoat solution for our application.

There are two other eminently practical reasons for preferring the precoat based on aqua regia over the one based on n-butanol. First, n-butanol presents a fire hazard when the anodes are dried, and it leaves a pyrophoric residue on the anodes. When the oven door is opened and the hot anodes are suddenly exposed to air, they sometimes catch fire. Losing test anodes in the laboratory to fire was a recurrent nuisance; losing two racks of 8 full-sized anodes to fire was rather more than a nuisance. Second, alcohol based precoat have limited shelf life, particularly after they have been used. The alcohol and traces of Ti^{+3} produced by corrosion of the Ti metal substrate reduce the Ir^{+4} in the precoat solution. First the solution changes from opaque red-brown (the color of Ir^{+4}) to sickly yellow-green (the color of Ir^{+3}), and then a black precipitate of Ir metal forms. At that point, the solution is fit only for reprocessing to try and recover the Ir value. As iridium is a precious metal, the precoat solution cannot be wasted in this way.

Thus far, there is no indication that we will need to go back to butanol based precoating solutions. It is encouraging that a change as simple as adding 2% nitric acid seems to afford an improvement in the quality of the precoat.

6. Improved sealing coat and slurry coat

The introduction of antimony as the doping element in the overcoat at the beginning of this project comprised the largest improvement by far in the composition of the oxide coat. The use of antimony as the doping element in the overcoat in place of niobium allows the slurry coat and overcoat to be baked-on under much milder conditions than would otherwise be required. The Sb-doped titanium dioxide that comprises the cement is conductive even when baked in air.

Other than that, the slurry coat was optimized by optimizing the coating procedure, as summarized in Section 4. The sealing coat worked well from the start, and was little modified. Mostly, we figured out how best to prepare it.

7. Attempts to improve the overcoat

During the first two years of this project, we measured N_{OH} but occasionally, while working to improve the current yield. When we did measure N_{OH} , sometimes we obtained reasonably good values: $2\text{--}3 \times 10^{-16}$ using p-cresol and up to 6×10^{-16} using benzaldehyde. At other times the results were much worse: $< 10^{-16}$ using benzaldehyde.

During the third year of the project, in June 2000, we turned our attention to improving N_{OH} . We started determining N_{OH} for many tail electrodes, and obtained disappointing results, mostly $< 10^{-16}$. We concluded that something was going wrong: either we were somehow making worse electrodes, or somehow our test procedure was off, giving us poor results.

We set out to identify the problem and correct it. We did indeed find some ways to improve N_{OH} , but the improvements were not very large; the values recorded rarely exceeded 1.2×10^{-16} .

For example, we realized that significant Schottky barriers probably existed between the layers of coating that we applied to our anodes. When current flowed from fiber-to-fiber in a cross-bundle direction, the Schottky barrier added-up, producing a poor electrical connection between many of the fibers and the current collector (a piece of heavy Ti-wire that the tail electrode was mounted on; see Figure 2). This problem was corrected by pressing the tail electrode against a strip of Ti-sheet which then served as the current collector, and the values of N_{OH} became larger and more reproducible. This improved arrangement closely approximates contact of the fibers with the Ti-plate in the full-sized electrodes; therefore, we succeeded in making our laboratory test methods more realistic, but failed to come up with anything that would improve performance of the full-sized electrodes.

During this period, we tried better defining and varying all sorts of details in the electrode coating procedure in trying to improve N_{OH} . The result was a substantial inventory of tail

electrodes with well documented production histories.

Finally, we realized that using benzaldehyde in sodium bicarbonate was giving us bad data, and switched to Butyl Carbitol in NaCl, with analysis by gas chromatography. Once the problems related to test procedure had been properly resolved, we proceeded to work through the test electrodes that we had accumulated.

Working through the accumulated test electrodes, we identified some factors that helped N_{OH} , albeit modestly, and other factors that hurt N_{OH} .

In the plus column, we found that overcoat prepared using antimony tartrate gave better results than overcoat prepared using antimony glycolate. This realization was somewhat of a relief; while use of antimony glycolate helps minimize formation of char, antimony tartrate is much easier to produce, and there is no antimony bearing chemical waste. As noted above, we learned that good electrical contact of the fiber to the current collector is critical; current cannot travel very far in the cross-fiber direction. We also learned that neither slurry coat nor overcoat needed to be steamed at a temperature higher than 200°C.

In the minus column, we learned that overcoat prepared with antimony tartrate has a finite shelf-life, and should be prepared fresh. We also learned that slurry coated electrodes should not be exposed to air above 200°C. To our surprise, Ti-fiber provided to us by the manufacturer which had been produced using improved manufacturing methods gave worse results than the “old” fiber that we had been using. This result will certainly be important when it comes to ordering more Ti-fiber for our needs.

Most of the things we tried proved to have no effect upon N_{OH} ; even these results were useful, as they told us what not to worry about. For example, used overcoat (which has a bit of slurry solids in it) works as well as fresh overcoat; therefore, the overcoat can be used repeatedly until it is used up, a realization that cause major implications in regard to waste minimization. We learned that moderate amounts of iron contamination in the blue powder did not significantly hurt the quality of the electrodes produced; therefore, we don’t need to invest extraordinary effort into keeping iron out of the blue powder and overcoat. Also, pickling the Ti-fiber before coating it in an effort to remove traces of iron that might remain from the fiber drawing process didn’t make any difference. Conversely, intentionally applying a small amount of iron to the fiber also had no effect. Independently varying the concentrations of antimony and titanium in the overcoat over a moderate range also had no effect; therefore, the exact composition of the overcoat isn’t critical.

In summary, we did not manage to improve N_{OH} very much. Our continuing research in this area is described in Volume II, Section 12.

8. Process operating conditions

8.1. Choice of electrolyte

Table 3 illustrates the effect of electrolyte used upon the current yield, all else being equal. The current yield using sodium perchlorate or monobasic potassium phosphate is much less than with sodium chloride. A repeat test using the same anode with sodium chloride electrolyte gave a slightly better current yield than before, indicating that the decreased current yield did not reflect degradation of the anode. Sodium nitrate and sodium borate electrolytes also give lower current yields than NaCl. Sodium bicarbonate gave highly erratic current yields, and sometimes COD actually increased during the run.

The reason oxyanions decrease current yield is presently unknown. One possibility is that they are oxidized to peroxy- species, which promptly decompose to produce oxygen. Another possibility is that they are strongly adsorbed to the surface of the working anode, blocking access of substrate molecules to the surface.

For obvious practical reasons, it is fortunate that NaCl seems to be the best electrolyte for this application. At the design current density of our anodes (25 mAmp cm^{-2} of plate area covered with fiber), 0.04N NaCl provides sufficient electrical conductivity, and was used most often as the electrolyte in our test work. The same conductivity would be provided by 8% sea water added to an initially nonconductive waste water. The primary disadvantages of NaCl are its corrosiveness and production of sodium hypochlorite as a reaction byproduct. Sodium hypochlorite is even more corrosive and may cause side reactions that confuse the data; for example, p-cresol cannot be used to determine N_{OH} in NaCl electrolyte, because hypochlorite with p-cresol more rapidly than p-cresol is oxidized at the anode.

8.2. Oxidation of the electrolyte

The formation of sodium hypochlorite as a byproduct when NaCl electrolyte is used is obvious from the smell and the large oxidation-reduction potential (ORP) of the solution. (ORP is easily measured using a platinum electrode in combination with a Ag/AgCl reference half-cell.) The amount of sodium hypochlorite can conveniently be determined by titrating the solution with sodium sulfite to an endpoint indicated by sudden decrease of ORP. In some cases, a substantial fraction of the NaCl initially present was found to have been converted to NaOCl.

If a series of samples are taken during a test of current yield, the current yield determined for successive time intervals usually decreases with time. A severe example of this effect is illustrated in Table 4. Repeating the experiment gave about the same results, indicating that the drop-off was not a reflection of damage to the anode. The simplest explanation is that the hypochlorite produced as a reaction byproduct is accumulating in the solution, and interfering with the reaction in the same manner as other oxyanions are known to interfere (Section 8.1). It is also possible that hypochlorite is being further oxidized to chlorite and then to chlorate, wasting current, and producing oxyanions that may interfere with the reaction even more.

Accumulation of hypochlorite may also be a factor in causing miniplates to have lower current yield than do tails. The current through a tail electrode is small in relation to the volume of electrolyte in the cell, and the concentration of hypochlorite builds up slowly. The current flowing through a miniplate is about an order of magnitude larger in relation to the volume of electrolyte in the test cell; therefore, the concentration of hypochlorite builds up much more

rapidly. By the time the first sample is taken, a substantial concentration of hypochlorite is already present, and the current yield determined is reduced thereby.

8.3. Effect of electrolyte pH

When a test is run in NaCl electrolyte with pH control, the pH climbs rapidly, peaks above pH 9, then drops to a bit below 9, and finally stabilizes at that value. The initial rise is related to formation of NaOCl. Chloride is the conjugate base of a very strong acid (HCl with $pK_a < 0$) and has no tendency at all to hydrolyse. Hypochlorite is the conjugate acid of a weak acid (HOCl with $pK_a = 7.54$) and hydrolyses to produce some HOCl, releasing hydroxide ion and increasing the pH of the electrolyte.

The pH of the electrolyte is also increased by the formation of acid at the anode, and base at the cathode. Because the anode is a porous mass of fiber, some amount of the acid produced hides out among the fibers, causing a local decrease in pH. Meanwhile, an equivalent amount of base is released to the bulk electrolyte (because the cathode is smooth), increasing pH in the bulk electrolyte. This component of the pH change is easily eliminated by ensuring good flow of electrolyte through the anode fiber, as will be the case in a full-sized water treatment unit.

The pH change is easily controlled by using a pH controller to control a peristaltic pump that adds a HCl to the electrolyte as needed to maintain stable pH. We found that running in NaCl electrolyte, pH near 5.5 provides the best current yield. At pH 5.5, 99% of the hypochlorite is present as HOCl, an uncharged species with no particular tendency to accumulate at the face of the anode and interfere with the desired oxidation of organic substrate. The exact value of pH is not important below about pH 6.5.

The dramatic effect of pH control was demonstrated in a test using a miniplate anode and Hastelloy cathodes in a cell provided with forced flow of electrolyte. With no pH control and NaCl electrolyte, the 0-10 minute current yield was 25% and the 10-30 minute yield 14%. When the test was repeated with pH controlled at 5.5, the 0-10 minute yield was 37% and the 10-30 minute yield was 32%.

8.4. Damage by fluoride

Hydrogen fluoride is the only substance able to damage titanium metal at low concentration, and we have seen damage to our electrodes in a few cases when we ran solutions that we knew to contain fluoride salts or organic fluorine compounds. However, the amount of fluoride in fluoridated tap water appears to have no effect.

For the time being, our recommendation to potential users will be not to put wastewaters that contain fluorine compounds into our water treatment units. In the long run, we expect to develop operating procedures that will allow the process to be used in the presence of a modest amount of fluorine. Two ways of controlling damage by fluoride have been identified, and will be investigated experimentally as part of our continuing research effort:

1. Fluoride is corrosive to titanium metal and titanium oxide because it complexes titanium

ions, sharply increasing the solubility of TiO_2 . The formation of a titanium fluoride complex, whether in solution or at a TiO_2 surface, involves displacement of hydroxide by fluoride; therefore, increasing pH offers a simple way of blocking the harmful influence of fluoride.

2. Several metals and semimetals form very stable complexes with fluoride in solution. There will probably be applications where fluoride appears in the waste water intermittently. In such cases, it may be possible to protect the anodes from damage by dosing just the water that is contaminated with fluoride with a soluble compound of a fluoride complexing metal at a concentration large enough to tie-up the fluoride.

These approaches will be tested as potential users provide us with samples of their waste waters to test in our laboratory using tail electrodes or miniplates.

8.5. Fouling of the anode

Several metals have soluble lower oxidation states, and insoluble higher oxidation states; that is, the higher oxidation state cations form insoluble metal oxides or hydroxides. These metals include Cr, Mn, Fe, Co, Sn and Pb. If these metals are present in the waste water as the relatively soluble ions of lower oxidation state, they will be oxidized to higher oxidation states, and insoluble metal oxides may deposit on the anode, fouling it. Some metal oxides are conductive or semiconductive, and may poison the anode by favoring generation of oxygen at potential much too low to generate hydroxyl.

Of these metals, iron is by far the most common. In fact, iron and manganese in the +2 oxidation state are often present in ground water and well water. We have occasionally encountered iron fouling in our test work, and have sometimes intentionally fouled anodes. We discovered long ago that even severe iron fouling can easily be removed by soaking the anodes in oxalic acid solution or warm, dilute citric acid solution. Both acids readily dissolve “rust” deposits, and citric acid has the advantages of being nontoxic and noncorrosive to Ti-metal.

When we made a set of seven full-sized anodes for the NFESC prototype unit, the blue powder that went into making the coating slurry had been contaminated by iron through a mistake in processing. Not wishing to discard a sizeable inventory of blue powder (which represents a substantial investment of labor) we cleaned it as best we could using citric acid and hoped for the best. In fact, the current yield of these electrodes started out low, but gradually increased to about 25% as they were broken in. While the prototype was operating, the electrolyte had a greenish color which quickly faded and disappeared when the cell was powered down. When the cell pack was disassembled, the working faces of the cathodes were found to be covered with an adherent black deposit. Ashing a sample of the deposit decrease its weight by about 30%, consistent with a composition predominantly of metal oxides, hydroxides and carbonates. Titanium dioxide shed from the anodes surely comprised a large fraction of this deposit, but the material catalyzed decomposition of hydrogen peroxide, confirming the presence of iron oxides which also account for the dark color. The anodes were subsequently recoated for another reason using blue slurry without iron contamination, and the cathodes were cleaned. After recoating, the deposit on the cathodes was much thinner, and the had the same blue-grey color as

the anodes, immediately identifying its source and composition.

These observations suggest that the iron contaminating the oxide coat of the anodes was dissolving while the anodes were operating, and depositing on the cathodes along with “blue powder” and, perhaps, calcium carbonate, to form the black deposit. Iron has an unstable +6 oxidation state, the ferrate ion FeO_4^{-2} . The green color was probably ferrate or another highly oxidized iron species with similar properties, formed by oxidation of the iron contaminating the surface of the anode. The soluble species produced at the anode was then reduced at the cathode, contributing to the black deposit. This process suggests that any iron deposits on the anode will be dissolved and transferred to the cathode as fast as they form. Because a substantial amount of deposit can collect on the cathode before it interferes with operation of the cell and the cathode can easily be cleaned, iron fouling should not be a serious problem.

Table 5 presents our estimates of how severe the problems associated with fouling by various metals might be. They are based on a brief survey of the chemistry and corrosion properties of the various metals.

Metal oxides where the metal ions have partially filled d-shells often are conductive and are likely to be electrocatalytic for generation of oxygen. Contamination with these oxides may to some degree depolarize the anode, causing it to produce oxygen instead of hydroxyl. Metal oxides where the metal ions have a closed shell or closed subshell electronic structure usually are insulators, and probably will not be electrocatalytic, unless doped with other ions. The second column of Table 5 indicates which metal oxides are likely to be electrocatalytic based on electronic structure and other properties of the oxides which may be deposited. Metal oxides which cannot poison the anode should cause little trouble even if deposited.

Most metal ions of valence +1 or +2 are soluble at mildly acidic pH, as will exist at the surface of the anode. Metal ions of valence +3 and +4 generally precipitate as insoluble oxides or hydroxides. Metal ions of valence +5, +6 and +7 usually form soluble oxyanions. The third column of Table 5 indicates which metals are soluble in the highest stable oxidation state. If the highest oxidation state is soluble, the metal oxide will not deposit on the anode. The fourth column indicates which metals may have a soluble oxidation state that may be produced at high anode potential, but would not be soluble otherwise. Iron is predicted to dissolve as ferrate at high potential, and the observations described above appear to confirm this prediction. The same may be true of Co and Ni, but that remains to be confirmed. The fifth column indicates the reagent that should remove the metal oxide, if it deposits on the anode. We have already succeeded in removing iron deposits using citric acid, and most of the other metals should be easily removed as well. Only the platinum group metals Pt, Ir and Pd are likely to be hard to remove; even in that case, aqua regia may do the job without corroding the Ti.

The last column predicts the severity of the fouling problem predicted for each of these metals. Only the platinum group metals have the potential to cause severe problems, because these metals are strongly electrocatalytic and highly insoluble. Fortunately, it is unlikely that a waste water containing platinum group metals will be encountered; a waste water that contains Pt, etc., would likely be treated to recover the precious metal value first.

The iron group metals (Fe, Co, Ni) are rated as “Moderate”, reflecting our experience with iron. Tin and lead present a somewhat special case: they may foul the anode, but they are unlikely to exert much of a poisoning effect.

Practically speaking, we expect that fouling will occasionally be encountered and will need to be dealt with on a case-by-case basis, but do not expect that it will present a serious impediment to the practical application of this technology.

9. The cathode

9.1. Cathode composition

The electrochemical cell must have a cathode as well as an anode. Ideally, the cathode should

- (a) Not corrode in service.
- (b) Reduce oxygen dissolved in the electrolyte to water or, better yet, to hydrogen peroxide.
- (c) If the concentration of dissolved oxygen and mass transfer at the surface of the cathode are such that reduction of oxygen cannot consume the entire cathodic current, the cathode should reduce water to produce molecular hydrogen at a moderate negative potential.

Several cathode materials have been tested, including stainless steel, graphite, lead, tin, Sn-2.5Sb (lead free solder), silver, Hastelloy C-276 (nominally Ni-2.5Co-15.5Cr-16Mo-3.8W-5.5Fe), and Hastelloy C-22 (nominally Ni-2.5Co-22Cr-13Mo-3W-3Fe).

The first requirement - freedom from corrosion - is absolute. Running in NaCl electrolyte, stainless steel, lead, tin and solder corrode. Graphite cannot be fabricated into large thin plates, and other geometries would be bulky, heavy and expensive to fabricate. Silver is expensive.

Happily, the two Hastelloys exhibit excellent corrosion resistance in the NaCl electrolyte. We use HC-276 welding rod as anodes in test cells, and have observed minor corrosion only. The manufacturer (Haynes International) recommended HC-22 as being more corrosion resistant than HC-276, and the difference in cost is small. We made the cathodes for the NFESC prototype out of HC-22. Minor corrosion was observed, entirely limited to the electrochemically inactive back side of the two cathodes at the very top and bottom of the cell pack. This minor corrosion was largely eliminated by a minor design change. No corrosion at all is evident on the working faces of the cathodes.

The only complaints about Hastelloy C-22 are that it is expensive, and difficult to machine. While Hastelloy cathodes will be about three times more expensive than stainless steel cathodes, they will still be considerably less expensive to produce than the titanium anodes. Also, the cathodes just have to be cut, drilled, and degreased and they are ready to go. Chances are, the only reprocessing that the Hastelloy cathodes ever need will be to clean them.

In applications where chloride is absent from the electrolyte, stainless steel cathodes should serve just as well, at lower cost.

While the Hastelloys possess the essential corrosion resistance, none of the cathode materials tested offer satisfy the electrochemical requirements set forth above. For reasons discussed below, we doubt that we will find a better material for the cathode than Hastelloy C-22.

9.2. Operating potential of the cathode

The solubility of oxygen is too small for reduction of oxygen to handle the entire current at the surface of the cathode, and the reduction of water to hydrogen appears to be the main cathodic reaction. Unfortunately, none of the cathode materials tested appear to be usefully electrocatalytic for the production of H_2 , and the cathode generates H_2 with a large overvoltage.

Using a cathode composition that is electrocatalytic for generation of hydrogen would allow the cathode operate at much smaller negative potential, decreasing cell voltage and allowing a large reduction in the amount of energy consumed by the process. Unfortunately, the only material usefully electrocatalytic for generation of molecular hydrogen at moderate pH values appears to be black platinum, which would be hugely expensive, and would introduce a large risk of poisoning the anode with Pt.

SUMMARY AND CONCLUSIONS

This project advanced the state of our technology to the point that we are now preparing a prototype water treatment unit for shipment to the NFESC (Port Hueneme). The full sized electrodes for the unit have already been coated and are now being broken in and tested, while assorted minor problems are being resolved. The electrodes are now performing like our best miniplates ($\epsilon = 30\%$, $N_{OH} = 1.7 \times 10^{-16}$ mole cm^{-2}) and are improving with break-in time.

Fiber embrittlement is no longer an issue, and the service life of the anodes is now longer than we can reliably measure using test electrodes in the laboratory. It is time to get units out into the field, to see how long the anodes last under realistic conditions; three months or longer seems possible. Current yield is now limited more by the geometry of the anodes and reactions with the electrolyte than by the quality of the anodes. Further research aimed at increasing current yield will emphasize these aspects of the problem. We know how to reprocess anodes that fail in service.

Our major disappointment was our inability to increase N_{OH} . Our continuing efforts related to increasing N_{OH} are outlined in Volume II, Section 12.4 of this report.

This project allowed us to develop and build several specialized devices for testing and characterizing our anodes which we would not have been able to acquire otherwise, and a detailed theoretical model of the electrode surface. Most of this capability was acquired toward the end of the project. These devices and the computer program will be extensively employed as

we continue research and development with our own resources.

The present state of the technology, our continuing research and development efforts, and our plans for transitioning/ commercializing the technology are discussed in Volume II of this report, together with some results from this project which were not disclosed in the recent patent applications, and which we prefer remain confidential for the time being.

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APPENDIX 1 - Gray water treatment system for CVNX aircraft carrier

While this final report was being written, the Contracting Officer's Technical Representative (COTR) for this project at Carderock NSWS (S.R. Mangum) asked us to provide first estimates for a gray water treatment system design for the CVNX aircraft carrier, based on our technology.

Table 6 summarizes the assumptions our response was based on.

Table 7 describes a relatively large water treatment unit which would be appropriate for a large installation; we call this conceptual design "Model 4.0." The installation would consist of multiple units of this description. Model 4.0 represents two steps up in size from Model 3.10, which we are designing and building right now.

Model 3.0 is the existing unit that is going to Keyport, WA in a few weeks. Model 3.0 contains a single cell pack with 7 anodes and draws 252 amps at 6V. Model 3.10 will contain a single cell pack with 15 anodes, and will draw 570 amps at 6V. Model 3.20 will contain a single cell pack with 25 anodes, and will draw 950 amps at 6V. Model 4 will contain four cell packs, identical to the cell pack in Model 3.20, and will draw 950 amps at 24 volts. All of these units, from Model 3.0 to Model 4.0 will use exactly the same electrodes, which we are already producing for Model 3.0.

While Model 4.0 will be substantially larger than Model 3.10, we would be able to provide a prototype within 6 months of receiving an order. Aside from the power supply and assorted bits subcontracted to a local machine shop, we would be able to build Model 4.0 entirely in-house. The power supply would be special ordered from one of several companies that supply power supplies to electroplating shops.

Table 8 summarizes the size, weight, power requirements, and estimated costs for an installation appropriate to treating the entire gray water flow of a CVNX class ship. We have assumed that a single installation will serve the entire ship, but it would probably be more practical to have several smaller installations distributed throughout the ship.

The first column in Table 8 assumes performance that we think we can deliver using the electrodes that we will soon be producing for Model 3.10. The second column allows for a reasonable amount of future improvement in the performance of the electrodes, and represents an estimate of what the technology should be like a few years from now.

The estimates are based on the assumption that the gray water will be pretreated by centrifuging it, or putting it through a conventional filter of some kind. Simple, low cost pretreatment of this kind will remove particles and oil droplets, but will leave dissolved contaminants in the water. Therefore, the COD remaining in the pretreated water will be a substantial fraction of the COD of raw gray water; we assumed 1.0g/L for purposes of this calculation.

If the water is, in fact, pretreated using ultrafiltration, the COD in the pretreated water may be quite a bit lower. In this case, the size and cost of the electrochemical water treatment system

could be quite a bit smaller than described in Table 8.

Our COTR provided a list of specific questions. The questions which the tables don't answer fully are answered immediately below. The questions and our answers have been renumbered and edited to make for easier reading.

(1) Can your technology meet applicable wastewater treatment standards on the CVNX scale for BOD, TSS, and fecal coliform in addition to UNDS-type standards for metals, organics, total P and N, O&G, and COD?

The technology removes COD and, of course, $BOD \leq COD$. We are assuming that the pretreated water will contain 1.0g/L COD, and the treated water will contain 0.03 g/L COD and slightly less BOD. The longer you treat, the lower the final COD and BOD. We are assuming that suspended solids and dispersed liquids (i.e. oil) will be removed by pretreatment. As the process will produce some amount of hypochlorite as a byproduct, the treated water should be pretty well disinfected. Organics will be destroyed in proportion to COD, with aromatics and other unsaturated compounds being destroyed more rapidly than other organics; therefore, the more toxic sorts of organics should be preferentially removed. Some fraction of heavy metals might be removed by precipitation as insoluble oxides or by crudding out on the cathodes, but we wouldn't bet on it.

(2) Is pre- or post- treatment required?

We are assuming that suspended solids and dispersed O&G will be removed by pretreatment consisting of conventional (not ultra-) filtration or centrifugation; the additional cost and bulk of either of these processes should be minor compared to the electrochemical process that we have sketched in detail. Of course, the better the pretreatment, the cheaper it will be to polish the water electrochemically, so pretreatment should be optimized as the less expensive component. If the water is ultrafiltered, the electrochemical process would get quite a bit smaller and cheaper.

(3) Are there any serious concerns that might block shipboard application of the technology?

The three things that we worry about are:

(a) The reaction of organic substances remaining in the treated water with hypochlorite might produce trace amounts of chlorinated organic substances. The amount will be small in proportion to the COD in the treated water, and chlorinated aromatics will not be present, because all aromatics will be preferentially destroyed, from whatever source.

(b) More than a few ppm of fluoride in the water could damage the anodes. Aqueous fire fighting foam is one source of organic F compounds likely to be encountered on ships. While the fluorine present in AFFF is bound as organic fluorine compounds, electrolytic oxidation may release part of it as fluoride, which would attack the anodes. We will probably need to put on-line total-F sensors in the system and, whenever F is detected in the wastewater, divert the water flow temporarily, or else dose the water with an "antidote" that will complex the fluoride,

protecting the anodes.

(c) The coating we now use contains antimony as a minor albeit essential constituent, and a little bit of antimony might leach out into the water. We expect the amount leached to be small and to decrease rapidly with time (since the Sb is locked in the TiO_2 crystal lattice as a dopant), and Sb does not seem to be considered a particularly serious pollutant in any case.

These questions should be investigated further.

(4) What are the byproducts of treatment (e.g., solids, liquids, gases) and can they be handled in a shipboard environment?

The electrolytic process will produce hydrogen as a byproduct, which will be stripped and diluted using air moved by blowers and discharged overboard. The air will be moist, but that can be countered by blending it with relatively dry air from the ventilation system; indeed, ventilation air that would be discharged anyway could be used as the air supply. The air might also contain trace amounts of HOCl , and might thereby be corrosive if moist.

As noted, the treated water may and probably will contain some amount of hypochlorite, which will render it mildly corrosive (comparable to laundry waste water, probably).

(5) Can the system effectively treat nitrogenous and phosphorous components of shipboard wastewater?

Some fraction of N in the water might be converted to N_2 and thereby eliminated. We doubt that the process will have much effect upon P, although a little bit might precipitate out at the cathode as Ca-salts, etc.. These questions should be investigated.

(6) What is the potential to integrate the treatment of non-oily and oily shipboard wastes within the system; that is, can oily and non-oily waste treatment be combined? Can the system be applied to other UNDS-type discharges?

The electrochemical process has excellent prospects for treating oily waste water, once the oil phase has been removed by pretreatment. Centrifuging would be an appropriate pretreatment method. Thing is, the most soluble compounds in oil are aromatics and assorted polar compounds, most of which will be preferentially destroyed by our process. Thus, pretreated bilge water is should actually be easier to treat than pretreated gray water. To calculate size, weight, etc., we would need to know flow volumes and COD of the bilge water. Most organic compounds would be destroyed pretty well, including many of the priority pollutants. Cyanide is very easy to destroy.

The electrochemical process could also be used as the final treatment for black water, after all suspended solids have been thoroughly removed; for example, anaerobic digestion, coarse filtration, centrifuging, and finally electrochemical treatment.

(7) Is there the potential for water reuse after treatment?

Treated water should be perfectly well suited to the following applications:

- (a) Flushing toilets.
- (b) Swabbing decks, cleaning equipment, etc.
- (c) Firefighting.
- (d) Wash and first rinse in the scullery, but not the final rinse.
- (e) Wash and first rinse in the laundry, but not the final rinse.

In all of these applications, the major concern would be the slightly corrosive nature of the treated water, which might restrict it to polypropylene or glass piping. Better quality CPVC should work, too, but the cheap white stuff is attacked.

(8) What would labor requirements related to O&M be?

We have not estimated the labor required on ship, nor included it in the costs. Operational labor would be pretty much limited to keeping an eye on the system. Maintenance labor should be minor in a system that has been properly tested and qualified for shipboard use. The cell packs would probably need to be swapped out every few months, and the pumps in the units would have the normal maintenance problems. Also, filters would need to be replaced or backflushed occasionally. All of these labor items could certainly be minimized by fine-tuning the design, and it should be possible to wire in appropriate alarms that would indicate and pin-point problems, thereby eliminating the need for most preventive maintenance. It should be possible to back-flush the filters automatically.

(9) What are shipboard utility requirements?

Only electric power and blower air would be needed, and, of course, an exhaust duct for the air coming out of the process.

Alternatively, the air blowers could be replaced by air movers powered by compressed air; the amount of compressed air needed would be about 4% of the blower air volume indicated in Table 8; the other 96% of the air would, of course, come from the compartment. Air movers have significant benefits over blowers in regard to size, cost, and reliability, and air movers made of CPVC could be used in suction mode without any concerns related to corrosion.

Please note that we have ignored some things that can't be estimated until we have some dockside data; for example, it might be necessary to add a bit of acid or alkali to control pH, or to add a bit of flocculating agents, etc., to make the pretreatment work better. Also, we have not included or costed the pretreatment process. We are confident that pretreatment by centrifugation would not be bulky or expensive, but it does need to be tested.

Table 1. Composition of anode coatings

Layer	Composition (mole percent)	Solution used to apply
Ti-fiber substrate	Nominally pure Ti-metal	n/a
Precoat	70 IrO_2 – 30 $TaO_{2.5}$	Metal chlorides in 3N HCl
Sealing Coat	96 SnO_2 – 4 $SbO_{1.5}$	Metal chlorides in 3N HCl
Slurry Coat	96 TiO_2 – 4 NbO_2 cemented with 96 TiO_2 – 4 $SbO_{1.5}$	96 TiO_2 – 4 NbO_2 particles (“blue powder”) suspended in diluted overcoat
Overcoat	96 TiO_2 – 4 $SbO_{1.5}$	Solution of TiGlycolate and SbTartrate

Table 2. Effect of anode geometry

No.	Anode	Cathode	Electrolyte	Current Yield (%)
1	Tail made of 200 count Ti-tow	SS mesh	0.04N NaCl	53
2	Frame anode	same	same	16
3	Miniplat anode	same	same	13
4	Tail made of tow taken from frame anode 2	same	same	56
10	Tail made of 400 count tow	same	same	34

Table 3. Effect of electrolyte and cathode geometry on current yield

No.	Anode	Cathode	Electrolyte	Current Yield (%)
5	Minipla ^{te} anode	SS felt	0.04N NaCl	5
6	Minipla ^{te} anode	SS mesh	0.05N NaClO ₄	1.4
7	same	same	0.04N NaCl	14
8	same	same	0.054N KH ₂ PO ₄	1

Note: Electrolyte concentrations were adjusted to give approximately equal conductivity.

Table 4. Current yield vs. time

Time (min)	Current Yield (%; average)	Current Yield (%; interval)
5	36	36
10	32	28
20	23	13
30	18	10
40	16	9

Minipla^{te} electrode with stainless steel cathodes operating in 0.04N NaCl buffer without pH control.

Definition of terms by example: The “average” value of current yield reported for 30 minutes (18%) applies to the time interval 0-30 minutes, while the “interval” value (10%) applies to just the preceding time interval; that is, 20-30 minutes.

Table 5. Predicted fouling by metal ions

Element	Poisons anode?	Highest Oxidation State Soluble?	Dissolves at High Potential?	Specific Reagent to Remove	Predicted Severity of Problem
V	n/a	Yes	n/a	n/a	None
Cr	n/a	Yes	n/a	n/a	None
Mn	Yes?	Yes	n/a	n/a	Minor
Fe	Yes	No	Yes	Citric Acid	Moderate
Co	Yes	No	?	Dilute Acid	Moderate
Ni	Yes	No	?	Dilute Acid	Moderate
Cu	No	Yes	n/a	n/a	None
Ag	?	No	No?	Nitric Acid	Minor
Au	n/a	Yes	n/a	n/a	Minor
Zn	n/a	Yes	n/a	n/a	None
Cd	n/a	Yes	n/a	n/a	None
Sn	No	No	No	Nitric Acid	Moderate
Pb	No	No	No	Dilute Acid	Minor
Pt, Ir, Pd	Yes	No	No	Aqua Regia?	High

Table 6. CVNX installation – common assumptions

5,000 person crew
114 L (30 gal) gray water/ day/ person; that is, total flow = $568 \text{ m}^3 \text{ day}^{-1} = 23.7 \text{ m}^3 \text{ hr}^{-1}$
Water initially contains 1.6g/L BOD
Water pretreated by conventional filtration or centrifuging
Pretreated water contains 1.0g/L COD
Treated water contains 0.03 g/L COD
Conductivity going into electrochemical system equal to 8% sea water
Near term manufacturing technology assumed
150% overhead applied to direct costs of production
Power valued at \$100/MW-hr
Electrodes can be reprocessed 3 times
Duty cycle is 100%; that is, “one month” = 720 hours.
COD behaves like diethyleneglycolmonobutylether (Butyl Carbitol)

Table 7. Description of the Model 4.0 Water Treatment Unit

4 cell packs, each containing 25 anodes
Unit (minus power supply) measures 600 mm W x 1,800 mm H x 600 mm D.
Dry weight approximately 180 kg
Operating weight approximately 240 kg
Design power draw is 950 A @ 24 VDC (four cell packs in series)
Power supply efficiency is 85%
Power supply measures 600 mm x 600 mm x 600 mm
Power supply weights 130 kg
Sonoma Research can build it in house, except for the power supply
Order it today, and we can deliver it by Christmas

Table 8. Summary of CVNX installation size

	Near Term Performance	Improved Performance
<u>Critical assumptions:</u>		
Current yield (%)	50	70
N_{OH} (mole cm^{-2})	1.5×10^{-16}	6×10^{-16}
Electrode service life (months)	4	8
<u>Estimated size and cost:</u>		
Units for 5,000 person ship	70	35
Power (MW)	1.08	0.78
Floor space to install (m^2)	73	45
Compartment volume (m^3)	200	120
Equivalent water storage (hrs)	8.4	5.2
Dry weight (metric tons)	22	11
Operating weight (metric tons)	26	13
Blower air ($\text{m}^3 \text{min}^{-1}$)	100	50
Procurement cost (\$K)	4,270	2,140
Consumables (\$K yr^{-1})	2,100	560
Energy costs (\$K yr^{-1})	950	680
Storage for one year's supply of replacement cell packs (m^3)	48	12

Notes:

By “near term” we mean FY 2002.

The compartment is assumed to be 2.7 meters high.

“Weight” includes the power supplies.

“Equivalent water storage” is how many hours worth of water flow you could collect in a tank with volume equal to the compartment required by the system.

APPENDIX II - Patent Application filed with US-PTO and under PCT.

Regular Patent Application of
Oleh Weres and Henry Edward O'Donnell
for
**ELECTRODE AND ELECTROCHEMICAL CELL FOR WATER
PURIFICATION**

Related Patent Applications

None.

Statement regarding Federally supported research and development

Development of improvements disclosed herein was partly supported by the Strategic Environmental Research and Development Program of the United States Department of Defense under Contract N00167-98-C-0011.

Background of the Invention - Field of Invention

The invention disclosed is an electrode comprising Ti-metal fiber wound on to a Ti-metal plate with an electrocatalytic coating that allows operation at a potential large enough to produce hydroxyl free radicals and oxidize substances dissolved in water or an electrolyte solution, and an electrochemical cell including such electrodes. An improved electrode coating sequence and coating procedure are also provided, providing increased service life and good current yield. Made of different materials, electrodes of this geometry may also be used in other process applications, in a fuel cell or as battery plaques.

Background of the Invention - Description of Prior Art

In US Patent 5,419,824 Weres and Hoffmann provided an electrode comprising a titanium metal substrate covered with a thin layer of titanium dioxide doped with about 4 mole percent of niobium in the +4 oxidation state. The single d-electron of the Nb^{+4} ions enters the conduction band of the mixed metal oxide, making the mixed oxide an

heavily n-doped semiconductor. In US Patent 5,364,508 Weres and Hoffmann disclosed use of this electrode as an anode to generate hydroxyl free radical by oxidizing water and to oxidize organic substances dissolved in water. In US Patent 5,439,577 Weres and Hoffmann provided a water purification device utilizing the electrodes provided in US Patent 5,419,824 and an electrolytic cell wherein these electrodes are made by applying the doped titanium dioxide layer to titanium sheet, and assembled in a bipolar array.

A detailed electrode coating procedure was provided in US Patent 5,419,824. A “white slurry” coating composition was prepared, comprising hydrous titanium dioxide (the precursor of anatase pigment which has been precipitated from titanium sulfate solution and washed, but not dried or calcined) dispersed in water. The water soluble compounds diammonium bilactatotitanium (commercially available) and ammonium niobate were added in the correct proportions to cement the slurry and provide the desired level of Nb-doping. An “overcoat” solution was also used, comprising an aqueous solution of the same titanium and niobium compounds. The Ti-metal substrate was dipped into the “white slurry” composition, then baked in air at 400°C to dry and bake on the slurry. About three coats of the white slurry were applied in this way, followed by three layers of “overcoat,” which cemented the slurry coat. Finally, the electrodes were annealed at 650-800°C under hydrogen to reduce the niobium in the coating to the +4 oxidation state, conferring the desired semiconductive properties upon the electrode coating. Adding a bit of water vapor to the hydrogen inhibits hydrogen absorption into the Ti-metal substrate, and small electrodes in the form of disks or rods may be produced in this way. However, annealing plate electrodes under hydrogen warps them severely, and fiber electrodes are embrittled and practically destroyed. Therefore, the utility of the electrode coating method revealed in US Patent 5,419,824 is limited to producing small laboratory test electrodes. Also, electrodes coated in this manner fail after a few days of continuous operation due to passivation of the Ti-metal surface beneath the semiconductive oxide coat, making them useless for practical application. Even with periodic reversals of current, an electrode made of Ti-fiber cannot be operated in bipolar mode, because take-up of hydrogen while cathodically polarized embrittles and eventually destroys the fiber.

In US Patent 3,878,083 De Nora et al. provided a titanium electrode coated with a

mixture of iridium dioxide and tantalum pentoxide. In US Patent 4,839,007 Kötzt et al. provided a method of purifying industrial waste water using an anode comprising a Ti-metal substrate coated with tin dioxide doped (in the preferred embodiment) with antimony. This coating composition allows the electrode to operate at potential high enough to oxidize organic materials dissolved in water. In US Patent 5,364,509 Dietrich described a titanium anode with a two layer coating. The first coat comprises a mixture of IrO_2 and Ta_2O_5 , and the second coat comprises SnO_2 doped with Sb.

In US Patents 4,444,642 and 4,528,084 Hinden and Beer teach using a solution of iridium trichloride and HCl in an alcohol solvent to apply a protective precoat, noting that the solution should attack the Ti-metal substrate, producing a thick oxide layer comprising IrO_2 and TiO_2 , intimately mixed. This coating solution is strongly reducing and depassivates the Ti-metal surface, causing it to corrode. In trying to use this solution, we also noted that it spoils rapidly once used, probably because Ti^{+3} produced by corrosion of the Ti-metal reduced the iridium in solution, causing it to precipitate. US Patent 3,878,083 teaches application of a coating comprising IrO_2 and Ta_2O_5 using a solution of IrCl_3 and TaCl_5 in hydrochloric acid. This coating solution is very weakly oxidizing. Scanning electron microscopy of Ti-fiber electrodes that we precoated using a solution comprising H_2IrCl_6 and TaCl_5 in hydrochloric acid (which is more strongly oxidizing and thereby less corrosive against Ti than the solution recommended in US Patent 3,878,083) revealed that some fibers had thick coatings on them, indicating depassivation and corrosion of the Ti-metal substrate, while other fibers had very thin coats. Because the diameter of the fibers is small, corrosion, if it occurs, can dissolve a large fraction of the fiber's mass, and the thick mixed oxide coating produced fills in the grooves typically present in the surface of the fibers, decreasing their effective surface area.

In process electrochemistry, increasing electrode surface area improves the kinetics of the electrochemical process at low reactant concentration. Increased surface area also decreases the true current density at the surface in proportion, allowing the cell to operate at lower voltage and increasing the service life of the electrode. In batteries, increased surface area of the electrode plaques provides improved contact with the active material, improving energy storage efficiency. In practice, large surface area

process electrodes and battery plaques are very similar and their design is governed by much the same criteria, allowing technology to be usefully and easily transferred between the two fields.

In US Patent 3,895,960 Brown et al. provided an electrode plaque made by compressing and diffusion bonding iron fibers, attaching a current collector by mechanical means or by welding, and plating the entire assembly with nickel to provide the needed electrocatalytic surface properties. In Brown's Example 1, iron fibers with length:diameter ratio of about 1,900 were used to produce an electrode plaque with 95% porosity, 0.025 inch thickness, and specific area $100 \text{ cm}^2/\text{cm}^3$. In US Patent 3,835,514 Pollock provided a similar electrode plaque with L:D of 800 to 8000:1, porosity of 70 to 97% and a diffusion bonded bus connector.

In US Patent 4,331,523 Kawasaki described electrodes suitable for water electrolysis comprising a perforate current collector, preferably titanium expanded mesh or titanium perforated plate coated with platinum group metals, with a "fibrous assembly" pressed against it to provide large surface area. He noted that the fibrous assembly could comprise a diffusion bonded "web" of titanium fibers coated with platinum groups metals. (Here and throughout, we use the term "platinum group metals" to mean the metallic elements Ru, Rh, Pd, Os, Ir and Pt and also their oxides.) Kawasaki did not specify L:D, porosity or specific area of the "fibrous assembly" in his electrodes, but his examples suggest values similar to those taught in US Patents 3,895,960 and 5,294,319.

In US Patent 4,708,888 Mitchell et al. described an electrode produced by applying an electrocatalytic coating to a fine titanium expanded mesh, then spot welding or metallurgically bonding current distributor members (also coated Ti) to the coated mesh.

In US Patent 5,294,319 Kaczur et al. combined and improved upon the elements of US Patents 3,895,960 and 4,331,523 to provide an electrode comprising a mat of titanium fibers of at least two distinct diameters with length:diameter greater than 1000:1 coated with platinum group metals and spot welded to a similarly coated titanium plate.

Metallurgically bonded fibrous electrode structures as provided in US Patents 3,895,960 and 4,331,523 are poorly suited to our application because a slurry coating

composition would not penetrate into the structure of the electrode plaque and coat the fibers uniformly. The same is true of the electrode provided in US Patent 5,294,319 comprising fibers spot welded to a plate. The same problem would preclude reprocessing and recoating spent electrodes. Also, production costs would be high, and the electrodes would be highly susceptible to fouling by particulates in a waste water treatment application.

The electrode provided by Coin et al. in US Patent 5,783,050, comprising multiple layers of Ti-expanded mesh wound on a Ti-plate with an electrocatalytic coating applied to the assembly, appears to solve this problem. However, the surface area of the expanded mesh is not very large, and applying many layers of expanded mesh to provide a large surface area would make the electrode quite thick. The current needs to flow a considerable distance through electrolyte to reach all active surfaces throughout the thick mesh portion of the electrode. Because electrolyte conductivity in a typical waste water treatment application is small, an electrode with this geometry would operate with uneven current distribution, where most of the current is bunched at the outermost layer of the electrode.

The electrode provided by Morin in US Patent 4,680,100 comprises a thick tow of thousands of very fine nonmetallic fibers coated with a thin layer of metal and wound on a nonconductive plastic support member with electrical connectors attached to the ends of the tow using solder. This electrode cannot be made of titanium or another valve metal, because titanium cannot be plated on to a nonmetallic fiber substrate, and titanium fiber tow is not available with the very small diameter and very large fiber count disclosed. If Ti-fiber tow of this geometry were available, coating it by dipping and baking would both embrittle and cement the very fine fibers; in particular, attempting to apply a slurry coating would cover the tow with a crust leaving most of the fibers inside the tow uncoated and practically inaccessible to electrolyte. If a Ti-fiber electrode with semiconductive oxide coating could be made with this geometry, it would be practically inoperable. With the modest electrolyte conductivity typical of most waste water treatment applications, current would not be able to penetrate into the thick tow much below its exposed surface, and most of the fibers in the tow would remain inactive. Also, the resistance of the very fine titanium fibers would be so large that the

current would not travel more than a few inches along the length of the tow, causing most of the length of the tow to remain inactive. Conduction perpendicular to the fibers would be small, as the semiconductive coatings relevant to our application exhibit a contact resistance, effectively blocking current from penetrating more than a few fibers in the perpendicular direction. It would be difficult to solder electrical connectors to the ends of the tow, because solder doesn't wet the slurry coat. If a solder bond were achieved, the solder would be wetted by electrolyte and would corrode, contaminating the water being treated with tin and lead.

Summary of the Invention

While we believe the theoretical explanations set forth herein to be true, we do not wish to be bound by them.

Herein we improve upon the electrodes described in US Patent 5,419,824. A reformulated outermost oxide coating is provided (hereinafter called the "slurry coat") comprising fine particles of TiO_2 doped with Nb in the +4 oxidation state cemented with an infilling matrix of Sb-doped TiO_2 . Additional coating layers applied to the Ti-metal substrate before applying the slurry coat provide a long service life, and favor good current efficiency when the electrode is operated as an anode.

First, a "precoat" comprising IrO_2 and Ta_2O_5 is applied. The precoat is very stable and electrocatalytic for generation of oxygen at moderate anodic potential. It protects the anode from failure by passivation of the Ti-metal substrate beneath the slurry coat. Any current that reaches the precoat through cracks in the slurry coat is discharged at a relatively low potential by generating oxygen, and the potential of the Ti-metal surface never rises high enough to create an anodic oxide layer thick enough to impede operation of the anode.

A "sealing coat" comprising SnO_2 doped with Sb is applied over the precoat. The sealing coat adheres well to the precoat, and the slurry coat adheres well to the sealing coat. The result is a well adherent slurry coat with few cracks that extend through to the precoat. Minimizing the amount of current that leaks from the electrolyte solution directly to the precoat through cracks in the slurry coat minimizes the amount of current that is wasted by generation of oxygen. The sealing coat is itself capable of

operation at an anodic potential large enough to oxidize some substances. Thus, leakage of current from the electrolyte through the slurry coat to reach the sealing coat does not depolarize the anode to nearly the same degree as would leakage of current to reach the precoat. Thereby, a large fraction of the anode current actually passes through the outer surface of the slurry coat creating hydroxyl free radical, and the current yield of the anode is good. (Current yield is proportional to Chemical Oxygen Demand removed from the electrolyte, divided by the electric charge passed through the cell. At 100% current yield, passing 1 Coulomb through the cell would remove 0.083 mg of COD.)

Adequate service life and current yield require that most of the surface of the Ti-metal substrate be covered with an moderately thick semiconductive oxide coat, and “slurry coating” is the only practical way to accomplish this. Also, the “slurry coat” is believed to be ceramic-like in its microstructure rather than glass-like, whereby cracks tend not to penetrate the entire thickness of the slurry coat.

Herein we provide an electrode comprising Ti-fiber tow (preferably about 200 fibers, approximately 25 micrometers in diameter) wound around a Ti-metal plate. The electrode is easily manufactured by directly winding the tow on to the plate using a suitable winding machine. The Ti-metal fiber provides large active surface area, but the diameter of the fiber is large enough to allow coating without embrittlement or excessive cementation. Cementation that occurs is easily countered by simple mechanical means; for example, by sonication between layers of precoat and sealing coat, or by lightly rubbing and rolling the tow against the plate to separate the fibers between layers of slurry and overcoat. When the coating fails, poorly adherent material can be removed by sonication and the plates can be recoated. Because the fibers are not in any way fused together, good permeability is retained.

Anodes of this description are most conveniently stacked in alternation with flat plate cathodes, separating anodes and cathodes using a plastic coated fiberglass screen to prevent short circuiting. Compressing the stack presses the fibers against the Ti-plate providing good electrical contact along the entire length of the tow, and producing a thin reaction zone which favors even distribution of current over the surface of all fibers. Forcing flow perpendicular to the length of the tow provides good contact of the electrolyte with the coated fiber, and purges gas bubbles from between the fibers. This

electrode and electrolytic cell are well suited for the purification of waste waters by oxidation of organic compounds dissolved in the water.

Alternatively, electrical contact can be provided by securing the fibers to the edges of the plate by slipping a small extruded plastic channel over the edge of the electrode. This arrangement is useful when operating in more concentrated electrolyte with a physical gap present between adjacent electrodes.

List of Drawing figures

Figure 1 shows the multiple coating layers applied to the surface of the Ti-metal substrate, which together comprise the electrocatalytic coating of the electrode.

Figure 2 shows the physical structure of the electrode.

Figure 3 illustrates the method used to wind the Ti-fiber on to the Ti-metal plate.

Figure 4 shows in vertical cross-section an electrochemical cell that includes several anodes of the kind illustrated in Figure 2.

Figure 5 is a horizontal cross-section of the cell assembly.

Figure 6 shows a stack of electrodes bolted together between two end plates in preparation for coating.

Description of the drawings

The electrode consists of a titanium metal substrate with a multilayer metal oxide coating applied to at least part of its surface. The structure of the multilayer electrocatalytic coating, which is only a few micrometers thick, is schematically depicted in Figure 1. The substrate 10 is titanium metal. The “precoat” 12 is applied to the surface of the substrate, producing a thin layer substantially comprising a mixture of IrO_2 and Ta_2O_5 which might also contain some TiO_2 and iridium metal. Other precoat compositions containing iridium or another Pt group metal may be used; for example, a mixture of IrO_2 and TiO_2 or a mixture of TiO_2 and Pt. A “sealing coat” 14 is applied over the precoat, preferably comprising SnO_2 doped with Sb. The sealing coat acts as a primer that provides much improved adhesion of the “slurry coat,” shielding the precoat from contact with the electrolyte. The “slurry coat” 16 is the thickest of the layers coating the anode. Preferably, it comprises fine particles of TiO_2 doped with Nb in the

+4 oxidation state which renders the TiO_2 conductive, and said particles are cemented with a matrix of TiO_2 doped with Sb. The “overcoat” 18 is applied over the slurry coat to further cement and seal the slurry coat. The overcoat comprises TiO_2 doped with Sb or with Nb in the +4 oxidation state. The overcoat soaks into the slurry coat and cements it, become part of the slurry coat; for this reason, slurry coat 16 and overcoat 18 are depicted as overlapping in Figure 1. For clarity, Figure 1 depicts the structure produced by a single slurry coating cycle, typically comprising three applications of slurry followed by one application of overcoat. More typically, two or three coating cycles are applied.

The physical structure of the electrode is depicted in Figure 2. Electrode plate 20 is a rectangle of Ti-sheet. The edges of the plate are smoothed to prevent damage to the fiber, the corners are slightly rounded for safe handling, and one corner is rounded with a distinctly larger radius 22, allowing it to be used as an index for orienting the plates consistently during the coating process. Many turns of Ti-fiber tow 24 are wound around anode plate 20. The ends of Ti-fiber tow 24 are tied to anode plate 20 using tie holes 26. Flow holes 28 provide water flow paths perpendicular to the plane of the anode when the anode is installed in the cell illustrated in Figures 4 and 5. Assembly bolt holes 30 allow passage of the bolts that are used to assemble the cell. Current collector bolt holes 32 allow the copper bus bars that serve as current collectors to be bolted to the edge of the anodes.

The method of winding the Ti-fiber tow on to the Ti-plate is illustrated in Figure 3. A winding machine is conveniently made by modifying a metal-working lathe. The cross-feed platform is removed together with the tool holder assembly. A bracket is attached to the carriage and guide pulley 54 is mounted on it. The tensioner assembly 52 is attached to the lathe at the tail end. Tensioner assembly 52 preferably is the kind used in magnet winding machines. Anode plate 20 is bolted between two mounting plates 40A and 40B using machine screws 42 together with the appropriate washers and bolts. Machine screws 42 pass through assembly bolt holes 30 in the anode plates. Spindle pieces 44A and 44B are made of pieces of round aluminum rod machined half-round at one end only, allowing them to be bolted to mounting plates 40A and 40B. The other end of each spindle piece is round. Spindle piece 44A is clamped in the chuck of the

lathe. Spindle piece 44B has a conical depression 45 machined into its cylindrical end. The point of the tail stock center is pushed against cylindrical depression 45 by adjusting the ram, thereby securely mounting the plate assembly on the lathe in a manner that allows it to be rotated. Mounting plates 40A and 40B and spindle pieces 44A and 44B are conveniently made of aluminum.

The lathe is geared to provide the pitch desired and set to operate at a low speed. As the lathe rotates the plate assembly (that is, the entire bolted assembly comprising electrode plate 20, mounting plates 40A and 40B and spindle pieces 44A and 44B), the lathe carriage moves feed pulley 54 smoothly along the length of the electrode plate, and Ti-fiber tow 24A is evenly wound on to electrode plate 20 with the desired pitch. The rotation of electrode plate 20 pulls Ti-fiber tow 24A through the system. The Ti-fiber tow comes off spool 46, and passes over directing pulleys 48A, 48B and 48C which take it through a container of water 50. Tensioner 52 controls and evens out the tension of the tow. The water in container 50 contains a small amount of a nonionic wetting agent. Wetting the Ti-fiber tow eliminates the possibility of fire caused by friction or static electricity, and decreases frizzing and pilling. The lathe is provided with a motor power cut-off relay and two reed switches located so that the edge of the carriage will press against one of them when feed pulley 54 has reached the end of the interval to be wound, shutting off the motor. After the lathe stops the ram is backed off and the chuck loosened to release the plate assembly. Machine screws 42 are removed, mounting plates 40A and 40B are pulled-out from between electrode plate 20 and Ti-fiber tow 24 wound on to it. Then another electrode plate is bolted into place and the entire plate assembly is mounted on the lathe. The lead screw direction control lever is adjusted to reverse the direction of carriage travel, and the lathe is turned on to wind the second electrode plate with the opposite pitch and direction of motion. Before turning on the lathe, the plate assembly should be rotated so that the tow is coming off guide pulley 54 is approximately parallel with the plane of electrode plate 20, to avoid breaking the tow.

Figure 4 shows an electrochemical cell that includes several electrodes of the kind illustrated in Figure 2, serving as anodes. To make the figure legible, the cell is foreshortened in the vertical dimension, and the thickness of the electrode plates and other internal components is exaggerated. The anodes are as depicted in Figure 2,

comprising electrode plate 20, Ti-fiber tow 24 that has been wound on to it, and an electrocatalytic coating applied. They are installed in the cell in alternation with cathodes 60. Cathodes 60 have the same dimensions as the anode plates 20 shown in Figure 2, the same flow holes 28, assembly bolt holes 30, and current collector bolt holes 32. However, they cannot be made of titanium which would warp and become brittle from hydriding if used as a cathode.

Contact of Ti-fiber 24 with cathode plates 60 is prevented by separating means 62 placed between the anodes and the cathodes. One or two layers of a plastic coated fiberglass mesh similar to that used for window screens but coarser (9 threads per inch or 3.5 threads per centimeter) may be used as the separating means. The spacing between adjacent anodes and cathodes is set by end gaskets 70, which also seal the ends of the cell assembly against water leakage. Ethylene-propylene rubber (EPR) is a suitable gasket material. The plastic back wall of the cell 66 and front wall 66A are backed by metal pressure plates 68 and 68A. The entire stack is pressed together using threaded rods 72 and nuts 72A. Threaded rods 72 are insulated using plastic tubing 74 which keeps threaded rod 72 from short-circuiting anode plates 20 with cathodes 60. Driven by an external pump or other electrolyte circulating means, the electrolyte flows into 76A and out of 76B the cell through plastic tube fittings 86. Flow holes 28 in anode plates 20 and cathode plates 60 define channels 28A permitting the electrolyte to flow in a direction perpendicular to anode plates 20 and cathode plates 60 inside the cell. The size and placement of flow holes 28 favor an even distribution of the flow between the electrodes inside the cell. Several layers of interlocking mesh are placed between the plastic outer wall 66 and the adjacent cathode 60 to prevent electrolyte from bypassing the electrodes.

As illustrated in Figure 2, anode plates 20 and cathode plates 60 are not symmetrical. The end with current collector bolt holes 32 is longer than the other end. In the assembled cell shown in Figure 4, the anodes are installed with the longer ends of anode plates 20 protruding from the upper part of the cell, and cathodes 60 are installed with the longer end protruding downwards. Current collectors 78, preferably made of solder plated copper, are bolted between anode plates 20 using threaded rods 80, which pass through current collector bolt holes 32, and nuts 80A, and the stack of anode plates

20 and current collectors 78 is connected to positive pole 84 of a power supply. Current collectors 78 are likewise bolted between the protruding ends of cathodes 60 which are connected to the negative pole 82 of the power supply.

Figure 5 illustrates a horizontal cross-section of the cell assembly. For clarity, the electrodes and layers of mesh inside the cell and the external tube fittings are not depicted in this drawing. As was shown in Figure 4, back wall 66 and front wall 66A are backed by backing plates 68 and 68A and the whole assembly is held together by threaded rods 72 and nuts 72A. Plastic sidewalls 90 define the sides of the cell. Sidewalls 90 are attached to back wall 66 using bolts 94 and threaded inserts 96. Threaded rods 98 and nuts 98A press the front part of sidewalls 90 against the edges of front wall 66A, and O-ring cords 92, which sit in machined grooves along either edge of front wall 66A, provide a water-tight seal. The vinyl tape 100 is used to seal the joint between back wall 66 and side walls 90. Minor leaks that may occur at the corners of the cell assembly are sealed using an appropriate caulking compound or plumber's putty (not shown).

Figure 6 shows a stack of anodes bolted together between two end plates in preparation for coating. Several anodes 20A (comprising Ti anode plates wound with Ti-fiber) are bolted together using Ti-threaded rods 152, Ti-nuts 152A, and Ti-spacers 154, allowing them to be coated as a unit. (The Ti-fiber 24 wound on electrode plates 20 is not shown in this Figure for clarity.) An end plate 150 made of heavier gauge Ti-sheet and larger than the electrode plates is included at either end of the stack. End plates 150 keep the edges of electrodes 20A from resting on the floor of the furnace, etc., and effectively put each electrode "inside" the stack whereby they are all coated equally and uniformly. The spacers are conveniently made by cutting Ti-tubing into short pieces of uniform length (8-10mm). Ti-threaded rods 152 pass through assembly bolt holes 30 in the anode plate.

Detailed Description of the Invention - Improvements Needed Over Prior Art

In trying to improve upon the coating procedures described in US Patent 5,419,824 we discovered that annealing the electrodes under argon at 800°C would reduce the niobium in the coat, probably due to diffusion of Ti-atoms from the Ti-metal

substrate into the slurry coat. Eliminating the hydrogen anneal allowed plate electrodes to be produced, but fiber electrodes subjected to this high temperature anneal were still severely embrittled.

Eventually we hit upon using a “blue slurry” coating composition that would allow us to anneal at a lower temperature. Hydrous titanium dioxide slurry was washed and the appropriate amount of a water soluble niobium compound was added to it using a minimum amount of water. The resulting paste was dried and crushed, then baked under hydrogen above 800°C to reduce most of the niobium to the +4 oxidation state. It is believed that some of the titanium was reduced to the +3 oxidation state as well. The resulting blue, semiconductive solid was then ground in a ball mill, washed, and dried to produce “blue powder.” “Blue slurry” was made by mixing the blue powder with overcoating solution and water. Initially, the electrodes were dipped in blue slurry and baked in air at 400°C, but it was found that drying the electrodes under steam at 100-200°C, followed by baking under argon or carbon dioxide at 450°C produced better electrodes. (Steaming removes organic residues.) Multiple coats of slurry and overcoat were applied in this way, producing a well-cemented electrode coating comprising semiconductive particles of “blue powder” bonded by a nonconductive cement comprising TiO_2 doped with Nb^{+5} . Finally, the electrodes were annealed under argon at 650°C to render the coating fully semiconductive. It is believed that solid state diffusion reactions involving small amounts of Ti^{+3} present in the blue powder reduce the Nb in the cement to the +4 oxidation state, producing an operable electrode. Decreasing the annealing temperature to 650°C gave us fiber electrodes that were still noticeably brittle, but usable.

Finally we replaced Nb in the overcoat with Sb as the doping element. This change allowed the annealing temperature to be reduced to 450°C under an atmosphere of CO_2 , producing even less brittle coated fibers. The coating on these electrodes comprised semiconductive particles of TiO_2 doped with Nb in the +4 oxidation state imbedded in a semiconductive cement of TiO_2 doped with Sb, probably in the +3 oxidation state. We also tested an overcoat compounded using water soluble chelates of tin and antimony, whereby the cement comprised SnO_2 doped with Sb. The surprising and unexpected result was that electrodes prepared using a Ti/Sb or even a Sn/Sb

overcoat performed just like electrodes prepared using a Ti/Nb overcoat. It is believed that the electrochemical properties of these electrodes are dominated by the particles of blue powder, making them practically indistinguishable from electrodes with a coating that contains titanium and niobium only.

A way to prevent electrode failure by passivation of the Ti-metal substrate was provided in US Patents 4,444,642 and 4,528,084 whereby a “precoat” comprising IrO_2 and TiO_2 was applied to the Ti-metal substrate prior to application of an electrocatalytic coating of a different kind. In US Patent 5,364,509 a mixture of IrO_2 and Ta_2O_5 was applied to the Ti-metal substrate before applying the final layer of Sb-doped SnO_2 . We tested these precoats and others, applying them to the Ti-metal substrate, followed by the Nb-doped TiO_2 slurry coat described in US Patent 5,419,824. The electrodes so produced had good endurance, but poor current yield. This failure was not surprising. In US Patent 5,419,824 Weres and Hoffmann stated that Pt group metals should not be present in the electrode coating in catalytically significant amounts if the electrode is to be operable at a potential sufficiently positive to generate hydroxyl. It is believed that the slurry coat contained pores, fractures and holidays which effectively exposed the underlying Ir/Ta precoat to contact with the electrolyte. Most of the current flowed to and through the exposed precoat and was wasted generating oxygen bubbles. Little hydroxyl was produced, and the current efficiency of the electrode was small.

We thought that an intermediate “sealing coat” might act as a primer to improve adhesion of the slurry coat to the precoat. After screening various compositions, we found that a sealing coat comprising SnO_2 doped with Sb had the desired effect. Surprisingly, sealing coat prepared using the hydrated solid salt $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ works much better than a sealing coat of the same chemical composition prepared using the anhydrous liquid SnCl_4 .

With this three layer coating sequence, we finally achieved good endurance and good current yield. The pronounced synergistic effect of applying a layer of Sb-doped SnO_2 underneath the final layer of TiO_2 doped with Nb^{+4} and Sb was surprising and unexpected. No reference suggested using Sb-doped SnO_2 as an intermediate layer for this or another purpose.

As noted in the review of prior art above, corrosion of the Ti-metal fiber when

wetted with the precoating solution is undesirable because a large fraction of the thin fiber can corrode away, and large variations among fibers result when some but not all fibers are attacked. Also, at the low current density of interest in this application, a thick precoat is not needed. Finally, a precoating solution that corrodes Ti tends to spoil quickly, and spoilage gets expensive when iridium is being wasted. For these reasons, a thin precoat produced without corroding the Ti-metal fibers is preferable. Using H_2IrCl_6 instead of IrCl_3 as taught in prior art inhibits corrosion to some extent. By adding nitric acid to the precoating solution to more strongly passivate the surface of the Ti-fibers, we more thoroughly inhibited corrosion, producing a thin, uniform coating comprising a mixture of IrO_2 and Ta_2O_5 . Improved electrodes resulted, and used precoating solution compounded with nitric acid doesn't spoil. In some applications, instead of serving as a precoat, the improved coating of IrO_2 and Ta_2O_5 produced by adding nitric acid to the coating solution may serve as the sole or final layer of a coating sequence, thereby improving upon US Patent 3,878,083.

Detailed Description of the Invention - Preferred Embodiment

The cell assembly.

In the preferred embodiment, electrode plate 20 is nominally pure titanium (Ti-Gr.1 or Ti-Gr.2) 0.02inches (0.5mm) thick, and measures 8 x 18 inches (203 x 457 mm). Cathode 60 is made of a corrosion resistant alloy selected for the application; for example, 316 stainless steel (approximately Fe-17Cr-12Ni-2.5Mo-0.08C-1Si-2Mn), Ni-2.5Co-15.5Cr-16Mo-3.8W-5.5Fe (Hastelloy C-276) or Ni-2.5Co-22Cr-13Mo-3W-3Fe (Hastelloy C-22). Hastelloy cathodes are preferred if chloride is present in the electrolyte. Cathode 60 is approximately 0.025 inches (0.64mm) thick. The hardware used to assemble the cell (threaded rods, bolts, nuts, threaded inserts, etc.) is stainless steel.

The outer walls and side walls of the cell are made of 0.5 inch (12.7mm) polypropylene. The backing plates are 0.25inch (6.35mm) aluminum plate.

Ti-fiber and winding procedure.

In the preferred embodiment of the invention, the titanium fiber is a 200 count tow of Ti-fibers with a nominal diameter of 25 micrometers; that is, the fibers do not have a circular cross-section, but the cross-sectional area of each fiber equals a circle of 25 μ m diameter. The material is nominally pure Ti, preferably Ti-Gr.1. The detailed coating procedure below is described in application to this tow, and the number of coating cycles, slurry concentration etc., might need to be adjusted if a different tow is used. Similarly, gas and water flow rates are sized for a 40 liter furnace chamber.

The tow is conveniently produced using the composite drawing method provided in US Patent 3,394,213. Ti-fiber tow of this kind is commercially available in the United States and in Europe. The Ti-fiber tow is wound on electrode plate 20 with a pitch of 20 per inch or 1.27mm; a different pitch may be needed to provide a smooth layer of fiber if Ti-fiber tow of a different fiber count or diameter is used.

The width and thickness of mounting plates 40A and 40B and the tension setting of tensioner 52 together determine the tension of the Ti-fiber tow after it has been wound on to electrode plate 20. In practice, one must take care that the Ti-fiber is not wound too tightly. If the Ti-fiber is too tight, it will bow the electrode plate 20 after the mounting plates 40A and 40B are withdrawn. Removing mounting plates 40A and 40B provides slack to the Ti-fiber, and the amount of slack increases with both the thickness and the width of the mounting plates. When winding electrodes 8 inches (203 mm) wide, mounting plates made of 3/32 inch (2.4 mm) aluminum sheet with a width of 6 inches (152mm) give good results with the tensioner set at about 35 ounces force (10 newtons).

Coating procedures employed and electrodes produced

The electrodes are mounted in a rack as shown in Figure 6, and coated employing the procedure presented below. The quality of the electrodes produced is quite sensitive to the pH, concentration, etc., of the slurry coating composition ("Blue Slurry") and the overcoating solution. The Blue Slurry and the overcoating solution should be prepared just before use.

The performance characteristics of newly coated anodes improves over the first few days of operation. New anodes may be "broken in" by operating for 2 to 4 days in

0.1N NaCl at the “design” current density of 25mA cm^{-2} referred to the surface area of the anode plate covered with the Ti-fiber.

Numerous electrodes of various sizes have been produced using this procedure with current yield ranging 20-50% and apparent surface concentration of hydroxyl ranging 1 to 2×10^{-16} mole cm^{-2} . (The latter parameter dominates the kinetics of the oxidation process at low reactant concentration.) The electrodes were tested by oxidizing diethyleneglycolmonobutyl ether in 0.04N NaCl while monitoring decrease in COD to determine current yield, and by determining the starting compound by gas chromatography to determine the surface concentration of hydroxyl. These electrodes can be operated for several weeks at 100mA cm^{-2} (that is, 4 times design current density) before decreasing current yield is noted.

EQUIPMENT NEEDED FOR COATING

1. A drying chamber, where the electrodes can be exposed to a constant stream of air at about 90°C to dry them. Provide a wet scrubber to collect any acid vapors that may be generated before they are released to the atmosphere.
2. A thermostated steaming chamber able to maintain 200°C temperature with provision for a controlled flow of liquid water into the chamber to generate steam. The steaming chamber should be equipped with an internal fan to vigorously circulate the atmosphere inside, means for introducing a purge stream of CO_2 or air, and a condenser to condense the steam flowing out of the chamber.
3. A thermostated furnace able to maintain 450°C temperature with provision for a controlled flow of liquid water into the chamber to generate steam. The steaming chamber should be equipped with an internal fan to vigorously circulate the atmosphere inside, means for introducing a purge stream of CO_2 or argon (useful for fire suppression), and a condenser to condense the steam flowing out of the furnace.

APPLICATION OF PRECOAT

Use “Precoating Solution 70 Ir - 30 Ta / 3N HCl” described below.

Dip the anodes into precoat solution and let excess drain.

Dry in the drying chamber.

Bake in the furnace in air at 400°C for 5 minutes measuring time from when furnace temperature reaches 400°C after inserting stack of electrodes and closing the door.

Repeat the steps above for a total of four cycles.

APPLICATION OF SEALING COAT

Use “Sealing Coat Solution 96 Sn - 4 Sb / 3N HCl” described below

Dip the anodes into sealing coat solution and let excess drain.

Dry in the drying chamber.

Repeat the steps above for a total of four cycles.

Bake in air at 400°C for 10 minutes, measuring time from when furnace temperature reaches 400°C after inserting stack of electrodes and closing the door.

Remove from furnace and cool to room temperature using a fan.

The fiber may come out of the seal coating procedure somewhat stuck together. For the best results, after cooling disassemble the stack and rub Ti-fibers gently with your fingers to loosen them, then reassemble the stack for slurry coating.

The coating procedure comprises application of multiple layers of slurry coat and overcoat. Good anodes are produced by the coating sequence 3 x (3xS,O); that is, three slurry coats followed by one overcoat, with the entire sequence repeated a total of three times.

APPLICATION OF SLURRY COAT AND THE OVERCOAT

Use “Blue Slurry Coating Composition BS TiSb₄” described below.

Stir the slurry to make it uniform.

Set steaming chamber temperature to 200°C.

Dip anodes in the slurry.

Place anodes in the steaming chamber.

Turn on water flow into steaming chamber at 24mL/min, and steam 40 minutes or as long as needed to completely dry the anodes.

Remove electrodes from steaming chamber and immediately dip them in water.
(The thermal shock counteracts cementation of the fibers.)

Set furnace temperature to 450°C.

Set inert gas (Ar or CO₂) flow into furnace at 3L/min.

Place electrodes in furnace for 40 minutes, measuring time from when furnace temperature reaches 450°C after inserting stack of electrodes and closing the door. Gas flow should be reduced to 1L/min after the door has been closed and temperature starts to climb.

Remove electrodes and cool rapidly using a fan.

The overcoat is applied exactly like the slurry coat, using the procedure described above with “Overcoat Solution TiSb4” in place of the “Blue Slurry Coating Composition.”

Composition of coating solutions

The composition of Precoating Solution 70 Ir - 30 Ta / 3N HCl is:

3N HCl

13.1mM TaCl₅

30.6mM H₂IrCl₆

0.3N HNO₃

2g/L nonionic wetting agent, preferably polyoxyethylene (10) isooctylphenyl ether

Deionized water as needed to make up the final volume.

Dissolve the TaCl₅ in the appropriate volume of 12N HCl, add part of the deionized water, add the H₂IrCl₆ solution, add the nitric acid and the wetting agent, and finally make up to the final volume with deionized water.

The composition of Seal Coating Solution 96 Sn - 4 Sb / 3N HCl is:

3N HCl

0.24M $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$

0.01M SbCl_3

2g/L nonionic wetting agent, preferably polyoxyethylene (10) isooctylphenyl ether

1mL/L of a silicone antifoaming agent which contains 10% polydimethylsiloxane

Deionized water as needed to make up the final volume.

First dissolve the appropriate amount of antimony trioxide (Sb_2O_3) in concentrated HCl to produce the solution of SbCl_3 . Then add part of the deionized water, add the solid $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ and stir to dissolve it, add the wetting agent and antifoaming agent, and make up to the desired volume with deionized water.

The composition of Overcoating Solution TiSb4 is:

0.24M TiGlycolate (mole ratio 1:1.33)

0.01M Sb Tartrate (mole ratio 1:1.25)

1.8g/L nonionic wetting agent, preferably polyoxyethylene (10) isooctylphenyl ether

1mL/L of a silicone antifoaming agent which contains 10% polydimethylsiloxane

Deionized water as needed to make up the final volume.

The source of Sb is a 0.1M antimony tartrate solution made by dissolving 0.1 mole of antimony triacetate (which is commercially available) in 1L of 0.125M tartaric acid. The source of Ti is a solution that we call "TiGlycolate(4/3)" prepared as described below, which contains the chemical components TiO_2 and glycolic acid in the mole ratio 1:1.33. This is approximately the lowest GA:Ti mole ratio to give a product that won't gel. Ti glycolate has the advantage over other water soluble Ti-chelates in that the glycolic acid represents relatively little COD, and is readily removed from the electrodes by exposing them to steam, whereby formation of char during the coating process is largely avoided. The actual concentration of Ti present in this solution will vary from batch-to-batch, and the actual amount used to prepare the overcoating solution needs to

be adjusted to give 0.24M Ti in the overcoating solution.

Add the antimony tartrate solution to a portion of the deionized water, add the required amount of TiGlycolate(4/3), and stir to dissolve. Add the wetting agent and the antifoaming agent, and make up to final volume with deionized water. Adjust the pH of the overcoating solution to 3.2 using ammonium hydroxide, and sonicate until clear.

The composition of the Blue Slurry Coating Composition BS TiSb4 is:
 33 volume % Overcoating Solution TiSb4 prepared as described above
 80g/L Blue Powder (prepared as described below)
 3.3g/L nonionic wetting agent, preferably polyoxyethylene (10) isooctylphenyl ether
 1.3mL/L of a silicone antifoaming agent which contains 10% polydimethylsiloxane
 Deionized water as needed to make up the final volume.

The amounts of wetting agent and antifoaming agent specified above are in addition to the amounts introduced with the overcoating solution. Mix the overcoating solution with part of the deionized water, add the wetting agent and the antifoaming agent, add the Blue Powder and mix until well dispersed, then make up to the final volume with deionized water.

Preparation of chemical materials not commercially available.

BLUE POWDER

The “Blue Powder” is a finely ground TiO_2 powder doped with 4 mole % Nb in the +4 oxidation state. Blue Powder is made starting with white anatase slurry, which is the precursor of titanium dioxide pigments made by the sulfate process and is commercially available. White anatase slurry is made by precipitating hydrous titanium dioxide from titanyl sulfate solution by heating it. The white anatase slurry has been washed to remove most of the sulfuric acid, but it has never been dried and certainly not calcined. Some sulfuric acid is allowed to remain in the commercial product to stabilize

it against gelling. The recipe below is directly applicable to a starting material that contains titanium equivalent to about 26 weight percent TiO_2 , and 2-4 weight percent sulfuric acid. A high purity commercial material that contains less than 50mg/kg of iron oxide is preferred. Our procedure for making the Blue Powder starts with a washing procedure to remove additional sulfuric acid.

1. Pour 5 gallons (19L) white anatase slurry into a 15 gallon (57L) plastic drum.
2. Add water to make about 13 gallons (50L) total volume and stir to disperse the slurry.
3. Let settle several hours then siphon off the supernatant water.
4. Repeat steps 1 through 3 two more times.
5. After third wash, refill and stir then let settle at least 12 hours.
6. Siphon off water and repeat step 5 one more time.
7. After completing step 6, pour into a five gallon (19L) tightly covered plastic bucket for storage. Let stand for at least one week.
8. Prior to using the washed slurry siphon off the supernatant water. The washed slurry should now contain 30-40 weight percent solids.
9. When ready to make fresh Blue Powder, siphon off supernatant water from the 5 gallon (19L) bucket then mix remaining slurry well.
10. Determine the solid content of the washed slurry by performing a gravimetric analysis (wherein the slurry is weighed, dried, and fired to orange heat in a crucible, and then weighed again after cooling) and calculate the weight of washed slurry needed to make the amount of Blue Powder desired.
11. To the washed white slurry add the amount of TMA Niobate Solution (prepared as described below) needed to introduce 4 mole percent Nb (relative to total Ti + Nb).
12. After mixing well, place in drying oven at about $90\text{-}95^\circ\text{C}$ until dry.
13. Grind until powder is visibly uniform.
14. Place the Nb-doped white powder into a four inch (10cm) diameter tube furnace with a quartz glass or stainless steel tube and purge with He or Ar to remove O_2 . Run exhaust gas through a bubbler containing 1N HCl to trap amine vapors released.
15. Set the temperature controller to 830°C and turn on the heat.
16. Replace the inert gas purge with H_2 and monitor until the gas coming out of the

furnace can be ignited.

17. For a 0.5 kg load of the Nb-doped white powder, heat under hydrogen at 830°C for 90 minutes.
18. Turn off the power and let furnace cool to less than 500⁰C then shift to either argon or helium for the rest of the cool down.
19. Once temperature is below 200⁰C, the furnace may be opened and the powder removed.
20. Place powder in a rubber lined 1gallon (3.8L) ball mill jar with 1/4 inch (6.35mm) alumina grinding balls.
21. Add 1.5g antifoaming agent (same kind as used in the coating recipes) and 0.15mL of wetting agent per 100gm of the calcined powder, which should now be a dark blue-grey.
22. Add filtered water to about 2/3 of the total volume of mill jar.
23. Grind for 48 hours.
24. After grinding is complete, strain out the alumina balls and rinse well to remove powder stuck to the balls.
25. Let ground powder and water settle for about 4 hours then siphon off supernatant water.
26. Place decanted slurry into drying oven at about 90 to 95⁰C and let dry.
27. Grind dried powder in a coffee grinder.
28. Store the dried Blue Powder in an air-tight container.

The Blue Powder may also be doped using ammonium niobate prepared as described in US Patent 5,419,824. Indeed, Blue Powder prepared using ammonium niobate seems to give slightly better electrodes, but ammonium niobate is rather harder to produce than TMA niobate.

PROCEDURE FOR MAKING “TiGlycolate(4/3)”

This recipe will produce a batch containing 1.92 moles of Ti.

1. Dilute 0.484L of titanium tetrachloride solution containing 21.5 weight percent TiO₂ and 38.5 weight percent HCl in about 4L of filtered water.

2. Place 7 pounds (3.2kg) of ice into a 5 gallon (19L) plastic bucket.
3. Mix 0.52 L of conc. NH_4OH with about 1 L of water and pour it over the ice.
4. While stirring, slowly pour the solution of titanium tetrachloride into the bucket.
5. Adjust the pH to about 6 using HCl or NH_4OH as needed.
6. Wash the precipitate by adding filtered water nearly to top of bucket and mixing, allowing precipitate to settle, then siphoning the supernatant water. Repeat this washing procedure a total of three times.
7. Centrifuge settled precipitate to dewater (700 to 1,000g).
8. Combine washed precipitate with 0.222 L of 70 weight percent glycolic acid in an appropriate container, then put into a hot water bath at 75°C until translucent (2-3 days).
9. Stir solution and allow to cool before using.

The pH of the mixture in step 4 should be in the range 5.5 to 7.0. Depending on the exact compositions of the solutions, it may be necessary to adjust the volumes used to provide the amount of Ti required by the recipe (1.92 g-moles) and give the pH desired.

PROCEDURE FOR MAKING “TMA Niobate”

This recipe will produce a batch of “TMA Niobate” containing 0.200 g-mole Nb and 0.200 g-moles of tetramethylammonium hydroxide.

1. Mix 26.85 g Nb_2O_5 with 84.42 g of K_2SO_4 and put mixture into a 250mL low form porcelain crucible or evaporating dish.
2. Under fume hood, add 43.6 g conc. H_2SO_4 and stir to mix.
3. Preheat box furnace to 650°C inside of exhaust hood.
4. Place crucibles into furnace for 15 minutes.
5. Half-fill a 1.2L blender with filtered water and set it to high speed.
6. Using crucible tongs, carefully remove crucible from the furnace, and slowly pour molten material into the water in the running blender.
7. Pour contents of the blender into a 1 gallon (3.8L) plastic pitcher, rinse blender

and pour rinse water into the pitcher.

8. Fill bucket with filtered water, mix, allow precipitate to settle for a few hours, and carefully pour off supernatant water. Repeat this washing cycle two more times.
9. Centrifuge precipitate to dewater.
10. Combine precipitate with add 72 mL of 25 weight percent $\text{N}(\text{CH}_3)_4\text{OH}$ in a plastic bottle and heat in hot water bath at about 90°C until clear.

Conclusions and Ramifications

Although the description above contains many specificities, these should not be construed as limiting the scope of the invention but merely as providing examples of some of the presently preferred embodiments. Thus the scope of the invention should be determined by the appended claims and their legal equivalents, rather than by the examples given.

The electrode coating sequence described herein may be applied to a Ti-metal substrate of any convenient geometry; for example, plates, woven mesh, expanded mesh, fiber, rod, wire, or a combination thereof. Other valve metals may be used as the material of the fiber tow or the support member; for example, Zr, Nb or Ta. Alloys of Ti or the other valve metals may also be used. The composition of the support member may be different from the composition of the tow, and the support member may be coated differently, or not at all.

By “disposed in a wound manner,” we mean that the fiber tow comprising part of the completed electrode looks like it was wound on to the plate, whether-or-not it actually was wound on to the plate; for example, the fiber tow might actually have been wound on an appropriate temporary support member, coated, and subsequently transferred to the plate with winding geometry preserved. While a single winding layer of tow, tightly spaced, is described in the preferred embodiment, a more loosely spaced wind or multiple winding layers may also be used. Different fiber counts and fiber diameters can be used. A fine Ti-wire or multiplicity of wires can serve as the Ti-fiber instead of a Ti-fiber tow comprising many fine fibers.

By “electrocatalytic coating,” we mean the entire multilayer sequence applied to the Ti-metal substrate. While our preferred embodiment includes a slurry layer

comprising TiO_2 doped with Nb in the +4 oxidation state and Sb, an outermost layer of another composition may be applied; for example, some other metal oxide composition that will produce hydroxyl free radical and oxidize substances dissolved in the electrolyte when a sufficiently large positive potential is applied to the electrode. The two layer coating sequence taught in US Patent 5,364,509 may be used. While Sb is preferred as the doping element for SnO_2 , other doping elements recommended for this purpose in US Patent 4,839,007 may optionally be used to make the SnO_2 usefully conductive. Doping elements may be used in combination.

By “coating composition” we mean either a solution or a slurry. The slurry coat may be cemented with Sb-doped SnO_2 in place of Sb-doped TiO_2 . In this case, the overcoating solution SnSb-4 is prepared using tin glycolate in place of titanium glycolate. The tin glycolate solution may be prepared exactly as described above for “TiGlycolate(4/3)”, but starting with a solution of tin tetrachloride in water in place of titanium tetrachloride. The “Blue Slurry Coating Composition SnSb-4” is then prepared using the SnSb-4 overcoat in place of the TiSb-4 overcoat. The slurry coat may be cemented using TiO_2 doped with Nb in the +4 oxidation state. In this case, Nb oxalate replaces Sb tartrate in the overcoating solution and the Blue Slurry. Niobium oxalate is prepared in the same manner as TMA niobate; at the last step, add oxalic acid (two moles per mole of Nb) instead of TMA hydroxide. After the electrodes are fully coated, anneal them under argon for at least one hour at 650°C to effect reduction of the Nb to the +4 oxidation state. Ta may also be used as the doping element in place of Nb. To dope the Blue Powder with Ta in place of Nb, use TMA tantalate in place of TMA niobate. To make TMA tantalate, dissolve tantalum pentachloride in 12N HCl, dilute the solution, adjust pH to 7 with ammonium hydroxide, centrifuge and wash the precipitate, and dissolve using TMA hydroxide. The cement can also be doped with Ta. Make overcoating solution using Ti glycolate and Ta oxalate instead of Sb tartrate or Nb oxalate. Make Ta oxalate following the procedure for TMA tantalate, substituting oxalic acid for TMA hydroxide at the last step. (The precipitate is slow to dissolve.)

In the preferred embodiment, nitric acid is added to the precoating solution. However, another passivating additive may be added in a concentration sufficient to inhibit corrosion of the Ti-fiber in the precoating solution; for example, salts of

molybdate, perchlorate, chlorate, dichromate, manganate, iodate or vanadate, or salts of Ce^{+4} .

In the preferred embodiment, the valve metal substrate of the electrode comprises Ti-metal fiber wound on to a rectangular Ti-metal plate, and the resulting electrodes serve as anodes. Electrodes with substantially planar geometry are preferred, because they may be disposed in a substantially parallel relation, preferably by being assembled in a stack in alternating sequence with planar counterelectrodes. A rectangular frame made of titanium metal strips may also be used as the supporting member, or another design. Optionally, the Ti-fiber tow may be coated in a continuous process or while temporarily wound on a corrosion resistant temporary support member, then wound on to a coated Ti plate.

A cathode or battery plaque of the same geometry can be made using a metal suited to the particular application; for example, by winding stainless steel fiber tow on to a stainless steel plate, or nickel fiber tow on to a nickel plate, or even carbon steel tow on a steel plate. Various electrocatalytic coatings may be applied; for example, nickel or copper applied by electroplating, electroless plating or other appropriate means.

Claims

1. An electrode comprising

a valve metal substrate,

a protective precoat layer containing at least one platinum group metal, and

an outermost metal oxide layer having a composition such that organic substances dissolved in an electrolyte solution will be oxidized when said electrode is polarized to a sufficiently large positive potential while in contact with said electrolyte solution,

wherein the improvement consists of further providing an intermediate layer selected to decrease leakage of current from said electrolyte solution directly to said protective precoat layer,

whereby the current yield of said electrode is improved.

2. The electrode of claim **1** wherein said outermost metal oxide layer comprises titanium dioxide doped with one or more additive metals selected from the group consisting of niobium in the +4 valence state, tantalum in the +4 valence state, and antimony.

3. The electrode of claim **2**, wherein said intermediate layer comprises tin dioxide doped to make it usefully conductive.

4. The electrode of claim **3**, wherein said platinum group metal is iridium.

5. The electrode of claim **4**, wherein said protective precoat comprises iridium dioxide and tantalum pentoxide.

6. The electrode of claim 3, wherein said valve metal is selected from the group consisting of titanium and titanium alloys.

7. The electrode of claim 3, wherein said outermost metal oxide layer comprises

particles of titanium dioxide and a cement binding said particles, wherein

said particles of titanium dioxide are doped with a doping element selected from the class consisting of niobium in the +4 oxidation state and tantalum in the +4 oxidation state, and

the composition of said cement is selected from the class consisting of tin dioxide doped to make it usefully conductive, and titanium dioxide doped with a doping element selected from the class consisting of antimony, niobium in the +4 oxidation state, and tantalum in the +4 oxidation state.

8. A method for producing an electrode having a valve metal substrate which includes the step of wetting said valve metal substrate with a solution of hydrochloric acid containing at least one compound of a platinum group metal, followed by drying and baking said electrode,

wherein the improvement consists of adding to said solution of hydrochloric acid a passivating additive in concentration sufficient to inhibit corrosion of said valve metal substrate when it is wetted with said solution of hydrochloric acid.

9. The method of claim 8, wherein said solution of hydrochloric acid contains an iridium compound and a tantalum compound.

10. The method of claim 8, including the subsequent step of wetting said electrode with a coating composition containing a substance chosen from the group consisting of

titanium glycolate and tin glycolate.

11. The method of claim **8**, including the subsequent steps of wetting said electrode with a coating composition containing organic substances, followed by exposing said electrode to an atmosphere substantially comprising steam,

whereby organic substances are removed, producing a better electrode.

12. An electrode comprising a metallic support member and metallic fiber having a surface, wherein said metallic fiber is disposed upon said metallic support member in a wound manner,

whereby an electrode is provided which has large active surface area and good internal electrical contact and is easy to manufacture.

13. The electrode of claim **12**, wherein said metallic fiber is a metallic fiber tow comprising a multiplicity of many fine metallic fibers.

14. The electrode in claim **13**, wherein at least part of said surface of said metallic fiber tow is covered with an electrocatalytic coating having an outermost surface composition.

15. The electrode in claim **14**, wherein said metallic fiber tow has a composition selected from the class consisting of titanium and titanium alloys.

16. The electrode in claim **15**, wherein said electrocatalytic coating has an outermost surface composition such that organic substances dissolved in an electrolyte solution will be oxidized when said electrode is polarized to a sufficiently large positive potential while in contact with said electrolyte solution,

whereby an electrode useful for water purification is produced.

17. The electrode in claim **16**, wherein said outermost surface composition comprises titanium dioxide doped with one or more additive metals selected from the group consisting of niobium in the +4 valence state, tantalum in the +4 valence state, and antimony.

18. The electrode in claim **14**, wherein said electrocatalytic coating contains at least one platinum group metal.

19. The electrode of claim **12**, wherein said metallic fiber comprises one or more fine wires having a surface and having a composition chosen from the class consisting of titanium and titanium alloys, and

at least part of said surface of said fine wires is coated with an electrocatalytic coating containing at least one platinum group metal.

20. An electrochemical cell having at least two electrodes, wherein

said electrodes include one or more anodes and one or more cathodes, and

at least one of said electrodes comprises a metallic support member and a metallic fiber tow having a surface, and

said metallic fiber tow is disposed upon said metallic support member in a wound manner, and,

said anodes and cathodes have a substantially planar geometry and

are disposed in a substantially parallel relation.

21. The electrochemical cell of claim **20**, wherein separating means are disposed

between adjacent anodes and cathodes, whereby electrical short-circuiting between said anodes and said cathodes is prevented.

22. The electrochemical cell of claim **21**, wherein

said anodes, said cathodes, and said separating means are pressed together, and

means to force electrolyte to flow through said cell are provided

whereby a desirable close spacing of said anodes in relation to said cathodes is provided, and electrolyte flows among said metallic fibers favoring good mass transfer at said surface of said metallic fibers.

23. The electrochemical cell of claim **20**, wherein

at least one of said anodes comprises a metallic support member and metallic fiber tow disposed upon said metallic support member in a wound arrangement, and

said metallic fiber tow comprises a valve metal selected from the group consisting of titanium, zirconium, niobium and tantalum and alloys of aforesaid metals, and

said metallic fiber tow is covered with an electrocatalytic coating having an outermost surface composition.

24. The electrochemical cell of claim **23**, wherein said outermost surface composition is selected such that organic substances dissolved in an electrolyte solution will be oxidized when a sufficiently large positive potential is applied to said anodes while they contact said electrolyte solution.

25. The electrochemical cell of claim **24**, wherein said outermost surface composition

comprises titanium dioxide doped with one or more doping elements selected from the group consisting of niobium in the +5 valence state, tantalum in the +5 valence state and antimony.

Abstract

An electrode with large active surface area is made by winding a Ti-fiber tow around a rectangular Ti-plate, and an electrocatalytic coating of three layers is applied. A precoat comprising a mixture of iridium dioxide and tantalum pentoxide is applied first, using a solution of the corresponding chloride salts in hydrochloric acid with some nitric acid added to inhibit corrosion of the metal. A sealing coat is then applied, comprising tin dioxide doped with antimony, in order to improve adhesion of the final oxide coat to the precoat. The third and final coat comprises particles of titanium dioxide doped with niobium in the +4 oxidation cemented with titanium dioxide that is doped with antimony. Anodes of this description are preferably assembled together with corrosion resistant cathodes in an alternating sequence, with a plastic coated fiber glass mesh placed between the anodes and cathodes to prevent short circuiting. When a sufficiently large voltage is applied across the cell, organic substances dissolved in the electrolyte will be oxidized.